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LVIII.—*The Latent Heats of Chloroform and Benzene and of their Mixtures Between 0° and 80°*

By JAMES FLETCHER and DANIEL TYLER.

A FAIRLY comprehensive investigation of the latent heats of binary mixtures of liquids has already been completed by one of the authors (T., 1911, **99**, 1633; 1912, **101**, 81, 1101), but the determinations were all made at the boiling points of the mixtures, and all the results obtained refer to these somewhat arbitrary temperatures. In this investigation the latent heats of various mixtures of two normal liquids, namely, chloroform and benzene, have been made at temperatures varying from 0° to about 80°, and the results furnish data for a complete study of the laws governing the latent heats of mixtures. It has been pointed out (T., 1911, **99**, 1633) that a mixture can be regarded as having two latent heats termed "latent heat at constant external pressure" and "latent heat at constant composition."

For a definition and explanation of these terms the reader is referred to the above-quoted papers. It may be mentioned that in the previous work only latent heats at constant pressure were experimentally determined, latent heats at constant composition being calculated from these results for a series of arbitrary temperatures. In the present paper a method is described for determining experimentally latent heats at constant composition at any temperature below the boiling point, and results are set forth for various mixtures of chloroform and benzene, two typically normal liquids.

If 1 gram of a mixture be placed in a vessel immersed in a thermostat and the pressure on the vessel be maintained equal to or slightly less than the saturation vapour pressure of the mixture, the liquid will completely evaporate, and in so doing absorb a certain amount of latent heat from the thermostat. This absorbed latent heat is precisely what we have measured. Of course, it will be clear that in the vaporisation the pressure does not remain constant, but gradually falls until the liquid is all evaporated, and a certain amount of external work is done against this pressure, and this external work is included in the absorbed latent heat. The results obtained for a given mixture at various temperatures should be comparable to the latent heats of a pure liquid at the same temperatures and evaporated under its own vapour pressure.

*The Method and Apparatus.*

The method adopted was similar in principle to that used by Griffiths and Marshall in their determinations of the latent heats of benzene (*Phil. Mag.*, 1896, [v], **41**, 1). As, however, our method differs from theirs in many respects it may be described here in full.

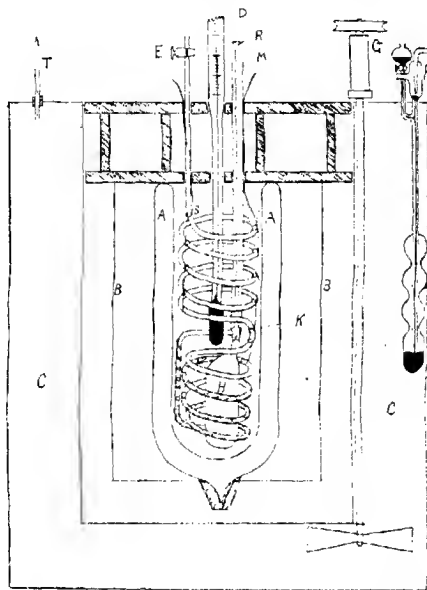
When 1 gram of chloroform is evaporated in a calorimeter containing 300 grams of water only about 60 calories are absorbed, causing a temperature change of only  $0.2^{\circ}$ . The measurement of so small a change with even a moderate degree of accuracy is quite impossible even on the finest graduated mercury thermometers. It is clear, therefore, that the ordinary method of direct measurement of the temperature change cannot be used. Instead of measuring the temperature change with a thermometer, we measure it indirectly by heating electrically the calorimeter by just so much as it was cooled in the vaporisation of the chloroform and measuring the current used in the heating. The current is measured by means of a silver voltameter, and we are enabled in this manner to interpret the temperature change due to the vaporisation of the chloroform in terms of the weight of silver deposited in the voltameter. It was found that a temperature change of  $1^{\circ}$  corresponds roughly with the deposition of about 0.3 gram of silver, and as this can be weighed accurately to less than 0.0001 gram it is thus possible to measure in this indirect manner temperature changes accurately to less than  $0.0003^{\circ}$ , supposing, of course, that the temperature after the experiment is just the same as before. In addition to this advantage we are by this method independent of:

- (1) Accuracy of the thermometer,
- (2) An exact knowledge of the specific heat of the calorimeter and contained liquid.

Further, by surrounding the calorimeter with a large bath maintained at a temperature the same or a little above that of the calorimeter, we can eliminate cooling corrections altogether or make them very small.

The calorimeter can best be explained by reference to the figure. The calorimeter proper consists of a large Dewar vessel, *A*, of about 400 c.c. capacity. This is contained in a cylindrical vessel, *B*, made of tinned sheet iron. This in turn is contained in a large double-walled copper tank, *C*, containing about 30 litres of water, and provided with a thermometer, *T*, a thermo-regulator, *F*, and a rotatory stirrer, *G*, which is actuated by a small electric motor. This outer bath of water is heated from below with burners, and maintained at such a temperature that the liquid in the Dewar

vessel remains at a constant temperature, as indicated by the Beckmann thermometer, *D*. The liquid the latent heat of which is to be measured is contained in the vessel *H*, which is provided with a tap, *K*, which by turning the tap-rod *R* can be opened or closed to the glass spiral tube. On the coils of this spiral tube is wrapped about 100 cm. of 0.02 cm. platinum wire fused on at *S* and *S'* to two pieces of copper wire of negligible resistance, and which are brought outside the calorimeter as shown. The spiral tube also serves as a stirring rod by arranging it so that it can be raised up



and down by means of a small motor and crank. The calorimeter is provided with a lid, as shown, which at first was made of wood, but later was made of hard asbestos board.

The Beckmann thermometer used in these experiments was one selected from six others, and was easily readable to  $0.001^{\circ}$ . To prevent sticking of the mercury thread it was constantly tapped during an experiment by a small electrical hammer. The absolute value of the readings was found by preliminary comparisons with a standard thermometer.



*The Electrical Apparatus.*

The general arrangement of the electrical portion may be described as follows. A storage battery of about five cells was connected with the heating coil in the calorimeter, with the voltmeter, and silver voltameter. The voltameter and voltmeter could be thrown out of circuit by switches, and thus allow a preliminary current to pass through the coil. This was used simply to adjust the temperature to the desired point. All the electrical contacts were soldered wherever possible, and the switches were of a heavy type, and made good contact.

The voltmeter used was a Weston standard voltmeter readable with accuracy to about 0.005 volt. The error in the voltage reading would not be greater on the average than 0.05 per cent. This instrument had been used in previous work, and always found trustworthy. It was tested before commencing this work, and found not to have altered during its use.

The voltameter was the usual form of silver voltameter, a plate of pure silver dipping into a solution of silver nitrate, which is contained in a platinum basin of suitable size, which forms the cathode.

*Working of the Apparatus.*

The liquid in the calorimeter may be either pure water or any other liquid of known specific heat and low vapour pressure. In the present work a series of determinations was made with water in the calorimeter, and then the whole series was repeated with pure aniline in the calorimeter. The Dewar vessel is first filled within a few centimetres of the top with a weighed amount of water or aniline. The spiral is placed in position, and the lid of the calorimeter put on. The Beckmann thermometer, having been previously adjusted to the desired temperature and the absolute value of its zero point determined by comparison with the standard, is now inserted into the liquid of the calorimeter so that its bulb lies within the coils of the spiral tube. The liquid in the calorimeter is heated by means of a shunted current to the desired point, and the liquid the latent heat of which is to be measured is introduced into the bulb of the spiral tube. This is done by aid of a closed dropping funnel which is provided with a long narrow delivery tube, which can be inserted into the bulb of the evaporating spiral. At the end of the delivery tube is provided an inner nozzle and a ground cap to prevent the loss of the adhering drop of liquid. The delivery vessel is filled with the liquid, and weighed by suspending it on the balance. The ground glass cap is then removed and also

the rod *R* of the tap (see figure), the long tube of the delivery funnel is inserted into the spiral, and an amount of the liquid run into the bulb *H*. The delivery vessel is then withdrawn, the ground glass cap and rod *R* replaced, and the delivery vessel weighed again. This gives the weight of liquid introduced.

The taps *K* and *E* of the spiral tube are closed. The motors which actuate the stirring of the liquid in the calorimeter and also in the water tank are now switched on, and observations of the Beckmann thermometer are made every two minutes. If the calorimeter is cooling, the temperature of the outer bath is raised, and vice versa. When the temperature of the calorimeter is constant or changes only very slowly, the rate of cooling per minute is carefully measured.

This enables one to make a small correction for the natural cooling or heating of the calorimeter during the course of the experiment. The end of the tube *E* is now attached by thick-walled rubber tubing to a strong water-pump and with a wash-bottle containing sulphuric acid to serve as an indicator of the rate of evaporation. The tap *K* is opened full and the tap *E* slightly, so that if it were opened wider the bubbling in the wash-bottle would proceed faster. This ensures that the vaporisation proceeds under the true vapour pressure of the particular liquid under investigation. The temperature as indicated by the Beckmann thermometer now slowly falls. After it has fallen a few tenths of a degree the current is switched on, and the temperature rises again. It is allowed to rise to a few tenths of a degree above the original temperature, and then the current is turned off. The temperature now falls below the original point, and by this time all the liquid has evaporated, which is indicated by the cessation of the bubbling in the wash-bottle. The current is now turned on again, and the mercury thread of the thermometer allowed to rise until on switching off the current it is brought back to the original point. Usually the initial and final temperatures are not absolutely identical, but differ by anything between  $0^{\circ}$  and  $0.03^{\circ}$ . The difference is carefully read off on the Beckmann thermometer, and a small correction made for it. This correction depends on (*a*) the assumed accuracy of the thermometric reading, (*b*) a knowledge of the specific heat of the calorimeter and contents. These are known very approximately, and since the total correction is itself very small, the error in the determination becomes negligibly small. After the evaporation has ceased the rate of natural cooling is again measured by the Beckmann thermometer, and is usually found to be the same as before the experiment. This, combined with the time of the experi-

ment, which is  $x$  so measured, gives the second and only other correction, and it can, with careful working, be made very small. The two corrections to the latent heat combined need not exceed one calorie, and as the error in the correction cannot amount to more than about 10 per cent., the error in the latent heat through this correction cannot be more than about 0.01 per cent. The time of the experiment varies. Near the boiling point of the liquid the whole of the liquid taken has evaporated in about eight to ten minutes, but at about the ordinary temperature it requires about an hour. Of course, it makes no difference whether the time of the experiment is long or short so long as the evaporation proceeds under its own vapour pressure, which was proved by repeating some experiments at little faster rates and obtaining the same result. The expression:

$$\frac{213.6 \times x \times V}{W} = L,$$

where  $x$  is the weight of silver deposited in the voltameter,  $V$  is the mean voltage,  $W$  the weight of the liquid taken, and  $L$  the latent heat.

*The Pure Chloroform.*—Commercially "pure" chloroform was taken, and distilled several times over an alkaline solution of potassium permanganate. It was then washed with water and dilute acid. It was dried first over calcium chloride, and then over phosphoric oxide, after which it was distilled in a fractionator and the first and last portions neglected; 700 c.c. distilled without the boiling point varying by more than 0.06°. Boiling point = 61.05°/756 mm. Specific volume at 20° = 0.67171.

*The pure benzene* was obtained by fractionating Kahlbaum's pure thiophen-free benzene over phosphoric oxide. Boiling point = 79.98°/751 mm. Specific volume at 20° = 1.13823.

The mixtures were made up by direct weighing of the constituents. The following mixtures were investigated, the compositions being always given in terms of the percentage of chloroform contained: 15.21, 29.42, 40.23, 53.04, 73.74, and 82.11. The chloroform and the mixtures were always kept in the dark, and care was taken to avoid change in composition of the mixtures through evaporation.

A series of determinations was made on the heat equivalent of the calorimeter, spiral, etc., (1) by the direct method of adding a known amount of cold water at known temperature into the calorimeter, and (2) by measuring the current required to heat the water and calorimeter through a given range of temperature which was measured on the Beckmann thermometer. The second method was

found to be the best, and gave the result 46.9 calories. This quantity need not be known with any particular accuracy, a few units variation making no appreciable error in the latent heat results. Then a series of determinations was made with the water calorimeter, the latent heats of the two pure liquids and of all the above mixtures being determined over temperatures varying from 20° to 75°.

The whole series was repeated with the aniline calorimeter. In determining the correction for the difference in the initial and final temperatures of an experiment, the specific heats of aniline as found by Griffiths (*Phil. Mag.*, 1895, [v], 39, 47) were used. Here again, however, the method of the experiments renders an accurate knowledge of the specific heats of the aniline quite superfluous.

### Results.

In the following tables are given the experimental values of the latent heats, together with the temperatures to which they correspond. In these tables the mixtures are given always in percentages of chloroform. Under *W* are given the results found when the calorimeter contained water, and under *A* the results when the calorimeter contained aniline. *T* is temperature, and *L* latent heat.

Pure Benzene.				Pure Chloroform.			
<i>W</i> .		<i>A</i> .		<i>W</i> .		<i>A</i> .	
<i>T</i> .	<i>L</i> .	<i>T</i> .	<i>L</i> .	<i>T</i> .	<i>L</i> .	<i>T</i> .	<i>L</i> .
20.5	101.00	22.7	103.83	20.6	62.85	22.0	63.09
29.3	102.77	43.7	99.86	19.3	63.32	31.8	62.19
29.0	102.65	51.5	99.16	21.7	62.55	43.3	61.05
28.8	102.96	59.9	98.29	28.57	62.09	51.5	60.31
40.1	101.13	60.7	98.07	29.57	61.85	52.0	60.20
52.2	99.14	69.4	96.68	19.1	61.32		
60.9	97.52	70.6	95.94	39.3	61.10		
68.2	95.97	71.9	95.43	10.9	61.01		
73.4	95.62			51.9	60.60		
72.9	95.71			52.6	60.01		
73.0	95.18						

15.24 per Cent. Mixture.				29.42 per Cent. Mixture.			
<i>W</i> .		<i>A</i> .		<i>W</i> .		<i>A</i> .	
<i>T</i> .	<i>L</i> .	<i>T</i> .	<i>L</i> .	<i>T</i> .	<i>L</i> .	<i>T</i> .	<i>L</i> .
21.6	98.52	31.7	97.28	19.8	94.20	22.4	93.84
30.2	96.83	43.5	95.09	30.2	92.99	31.9	92.10
41.9	95.25	51.6	93.62	40.3	90.86	43.4	90.61
51.6	93.70	59.8	92.30	51.6	88.72	51.6	88.93
68.9	91.07	69.6	90.64	68.7	86.55	59.6	87.60
68.7	90.93	71.8	89.95	68.0	85.69	69.9	85.92
73.0	90.24			72.8	85.79	71.9	84.81

40.23 per Cent. Mixture.				53.04 per Cent. Mixture.			
W.		A.		W.		A.	
T.	L.	T.	L.	T.	L.	T.	L.
21.6	89.15	31.9	87.93	19.9	82.33	22.6	82.86
30.2	87.73	43.2	85.69	30.1	81.98	31.9	82.94
41.0	85.95	51.6	84.64	40.7	80.25	43.1	80.83
51.5	84.76	59.4	83.51	40.8	81.04	54.1	79.01
60.1	83.01	70.9	81.20	51.5	79.29	60.0	78.28
67.1	81.71			59.3	78.58	70.5	76.98
				68.4	77.32		

73.74 per Cent. Mixture.				82.11 per Cent. Mixture.			
W.		A.		W.		A.	
T.	L.	T.	L.	T.	L.	T.	L.
21.6	75.55	31.8	74.07	19.8	71.86	22.2	71.18
30.1	73.83	43.2	72.53	30.0	70.28	31.6	69.71
40.5	72.46	53.3	71.07	40.2	68.72	43.1	68.95
51.6	71.17	59.7	70.13	52.0	67.80	52.7	67.40
51.6	71.15	59.6	70.15	59.5	67.04	59.5	67.24
59.3	69.40						

As will be noticed, the temperatures are somewhat irregular, as it was found difficult and inconvenient to make all the determinations for each series at regular and constant temperatures. In order, therefore, to obtain comparable results and at the same time to eliminate accidental errors in the determinations, the above figures have been plotted on a large sheet of cross-section paper. First the latent heats of each mixture were plotted against the temperatures, and the smoothed curves then drawn. It was found that these curves all came out quite straight lines. The water and aniline values were used together in drawing these curves, as both series separately would give the same smoothed curve. In the following tables are given the latent heats for regular intervals of temperature as read from the smoothed curves. The values at 0° and 10°, as also the values at the higher extremes of temperature, were obtained by extrapolating the curves. This was a perfectly safe thing to do, since the curves are straight.

Results for pure benzene.		Griffiths and Marshall.	Results for pure chloroform.	
Temp.	Latent heat.		Temp.	Latent heat.
0	167.51	167.65	0	64.85
10	165.89	165.47	10	63.95
50	164.26	163.89	20	63.05
50	162.65	162.22	30	62.17
40	161.05	160.71	40	61.29
50	89.44	89.14	50	60.40
60	97.84	97.56	60	59.51
70	96.23	96.00	61.27	59.40
80	94.61	94.40		
80.3	94.55	94.37		

For comparison the results by Griffiths and Marshall (*loc. cit.*) for pure benzene are also given. It will be noticed that our results are a little higher. The values at the boiling points (at 760 mm.) have been obtained by extrapolation. The boiling-point result for chloroform compares very well with the result 59.29 at 61.52° (=59.31 at 61.27°) found by one of us (T., 1911, 99, 1633) by an entirely different method.

The probable error of the results we consider not in general to be higher than  $\pm 0.1$  calories. In the following tables are given the results for the various mixtures investigated.

Temperature.	Latent heat.					
	15.24%.	29.42%.	40.28%.	53.04%.	73.54%.	82.11% of $\text{CHCl}_3$ .
0°	102.13	—	—	—	78.53	—
10	100.49	96.03	91.12	—	77.09	72.66
20	98.89	94.34	89.55	83.12*	75.65	71.50
30	97.20	92.62	87.97	81.93*	74.21	70.37
40	95.55	90.91	86.38	80.71*	72.79	69.24
50	93.93	89.26	84.80	79.49*	71.41	68.11
60	92.32	87.63	83.19	78.28	70.05	67.06
70	90.72	85.57	81.57	77.09	68.70	65.98
80	89.13	—	—	75.88	67.37	—

\* These results are probably slightly low.

Latent heats were next plotted against composition for each constant temperature. The curves obtained showed only slight curvature. From these curves values were read off at even composition. They are given in the following table:

Composition.	Latent heats at					
	20%.	30%.	40%.	50%.	60%.	70%.
10% $\text{CHCl}_3$ ...	100.75	99.25	97.55	95.98	94.44	92.69
20% $\text{CHCl}_3$ ...	97.32	95.79	94.09	92.45	90.80	89.05
30% $\text{CHCl}_3$ ...	93.82	92.28	90.43	88.81	87.26	85.65
40% $\text{CHCl}_3$ ...	90.00	88.46	86.63	84.98	83.45	81.76
50% $\text{CHCl}_3$ ...	85.98	84.44	82.70	81.13	79.55	78.05
60% $\text{CHCl}_3$ ...	81.78	80.20	78.67	77.15	75.70	74.29
70% $\text{CHCl}_3$ ...	77.32	75.85	74.47	73.07	71.70	70.39
80% $\text{CHCl}_3$ ...	72.68	71.34	70.18	68.94	67.70	—
90% $\text{CHCl}_3$ ...	67.92	66.76	65.78	64.72	63.66	—

In the previously mentioned investigation by one of us on the latent heats of mixtures of chloroform and benzene results were given for a series of temperatures which were the boiling points of the mixtures at pressures fairly near 760 mm. By extrapolating the values given in the above table we can obtain the latent heats at the boiling points, and thus compare them with the values previously obtained.

Composition.	Temperature.	$L$ .	$L'$ .
10% $\text{CHCl}_3$ .....	79.86°	91.51	91.1
20% $\text{CHCl}_3$ .....	79.03	87.57	87.9
30% $\text{CHCl}_3$ .....	78.13	84.36	84.6
40% $\text{CHCl}_3$ .....	77.15	80.46	81.1
50% $\text{CHCl}_3$ .....	75.95	77.16	78.2
60% $\text{CHCl}_3$ .....	74.60	73.18	75.0
70% $\text{CHCl}_3$ .....	72.81	69.96	71.6
80% $\text{CHCl}_3$ .....	70.48	66.49	68.3
90% $\text{CHCl}_3$ .....	67.00	63.00	64.1
100% $\text{CHCl}_3$ .....	61.45	59.38	59.29

The temperatures given in the second column of the above table were obtained from previous work. The values under  $L$  are the latent heats at these temperatures, and the values under  $L'$  the latent heats determined in previous work. An exact agreement between the two sets of values is not expected because the previously obtained results represent the latent heat plus a small extra quantity of heat required to expand the vapour from the volume at the vapour pressure of the mixture at the temperature considered, to the volume at the atmospheric pressure, work being done against the atmospheric pressure. The previously determined results should therefore be slightly greater than those determined by the extrapolation of the results obtained in the present work.

#### *Discussion of Results.*

The complete set of values of the latent heat of chloroform and benzene mixture enable us to answer the following questions:

(1) How does the latent heat of a mixture of two normal liquids vary with the temperature?

(2) How does the latent heat of a mixture vary with the composition when the temperature is constant?

In regard to the first question we may state at once that the latent heat at constant composition of a mixture of two normal liquids is, at least for temperatures at which the vapour pressure is less than atmospheric, a linear function of the temperature. In this respect, therefore, a mixture behaves exactly like a pure liquid. With regard to question (2) it was found on plotting the curves that they were very nearly straight lines. They were all just slightly concave to the composition axis. The deviation from the additive or linear function is shown by the following table, which contains under  $L$  the observed latent heats and under  $L$  (cal.) the latent heats calculated according to the linear function from the latent heats of the pure constituents at the same temperature. Under  $\Delta$  are given the differences or deviations from the additive.

Temperature.	Composition.	<i>L</i> .	<i>L</i> (cal.).	$\Delta$ .
20°	10% CHCl <sub>3</sub>	100.75	100.23	+0.52
	30% CHCl <sub>3</sub>	93.82	92.17	+1.65
	50% CHCl <sub>3</sub>	85.98	84.11	+1.87
	70% CHCl <sub>3</sub>	77.32	76.05	+1.27
	90% CHCl <sub>3</sub>	67.92	67.99	-0.07
40°	10% CHCl <sub>3</sub>	97.55	97.61	-0.06
	30% CHCl <sub>3</sub>	90.43	89.52	+0.91
	50% CHCl <sub>3</sub>	82.70	81.43	+1.27
	70% CHCl <sub>3</sub>	74.47	73.34	+1.13
	90% CHCl <sub>3</sub>	65.78	65.24	+0.54
60°	10% CHCl <sub>3</sub>	94.45	94.91	+0.44
	30% CHCl <sub>3</sub>	87.26	86.34	+0.92
	50% CHCl <sub>3</sub>	79.55	78.68	+0.87
	70% CHCl <sub>3</sub>	71.70	71.01	+0.69
	90% CHCl <sub>3</sub>	63.66	63.35	+0.31

The deviations, it will be noticed, are only small, and seem to become smaller as the temperature rises. We may state, then, that *the latent heat of a mixture of two normal liquids at constant temperature is approximately a linear function of the composition.* Probably with absolutely normal liquids the agreement with the additive law will be exact, and with less normal liquids, and particularly with liquids which form compounds or solvates when mixed, the deviations will probably be strongly marked.

Although these generalisations are based on one pair of liquids only there can be little doubt that these are quite normal, and form normal mixtures typical of this class of liquid. Moreover, one of the authors has already shown in previous work that the latent heats of the chloroform benzene mixtures at their boiling points show the same simple behaviour as do other mixtures (T., 1912, 101, 81).

The latent heats considered in this work consist, in part, like the ordinary latent heats of pure liquids, of external work done in the vaporisation.

Sufficient data are not available for the calculation of this external work, but in any case it is comparatively small, and does not vary greatly from one liquid to another, so that the generalisations arrived at will be scarcely affected by taking the external work into account.

It may be added finally that now the additive nature of latent heats for mixtures is established, the method of detecting solvates in mixtures of liquids described by one of us (T., 1912, 101, 1104) may be applied to results for mixtures at constant temperature.

#### Summary.

A method is described for accurately determining latent heats at constant composition of mixtures over a large temperature range.



The latent heats of pure chloroform and pure benzene, and mixtures of these liquids of varying compositions, have been determined between the ordinary temperature and the boiling points.

It is found that for any given mixture the latent heat is a linear function of the temperature, and for a given temperature the latent heat is approximately a linear function of the composition.

In conclusion, the authors thank the Chemical Society for a research grant, which has largely defrayed the cost of the work.

THE CHEMICAL LABORATORIES,  
THE UNIVERSITY, MANCHESTER.

### LIX.—*The Relation Between the Absorption Spectra of Acids and their Salts. Part I. Sodium Salts.*

By ROBERT WRIGHT (1851 Exhibition Scholar).

It is a matter of common knowledge that many acids show a marked colour change when their acidic hydrogen is replaced by a metal, such as sodium, which in itself is colourless. The various indicators used in acidimetry, for example, litmus or methyl-orange, furnish well-known examples of such phenomena. By the application of photography the investigations have been extended to the invisible regions of the spectrum, with the result that numerous substances (such as the phenols) are now known which show a marked change in their absorption spectra on the addition of sodium hydroxide. This change is most frequently ascribed to a variation in molecular structure taking place on salt-formation; the present investigations, however, seem to indicate that change in absorptive power can occur where such variation is hardly possible.

For the most part the examination has been confined to acids of a simple structure, where there is little possibility of atomic rearrangement taking place on neutralisation. Further, aqueous solutions were used throughout, so that any change in absorptive power which might be produced by alteration of the degree of ionisation would have its full effect. As many of the substances photographed have been previously investigated, the full absorption

curves have not been drawn, but the results are expressed by means of tables.

*The Fatty Acids.*—As will be seen from the table, these acids all show a decrease in absorptive power on salt-formation. This decrease is most marked in the case of formic acid, and grows less as we ascend the series. In the case of the substituted acetic acids, the spectra of salt and acid were practically identical. In this table, as in all others, the ionisation constant  $k$  of each acid is given; these constants were obtained from Kohlrausch's "Leitvermögen der Elektrolyte." The limits of absorption for 10 cm. and 1 cm. are given in wave-lengths.

TABLE I.

	10 cm. Spectrum transmitted to $\lambda$ .	1 cm. Spectrum transmitted to $\lambda$ .	$k$ .
Formic acid, $N$ .....	2520	2430	0.0214
Sodium formate, $N$ .....	2430	2330	—
Acetic acid, $N$ .....	2460	2355	0.0018
Sodium acetate, $N$ .....	2410	2320	—
Propionic acid, $N$ .....	2480	2360	0.0013
Sodium propionate, $N$ .....	2460	2335	—
$n$ -Butyric acid, $N$ .....	2500	2380	0.0015
Sodium $n$ -butyrate, $N$ .....	2480	2340	—
<i>iso</i> -Valeric acid, $N/10$ .....	2560	2390	0.0017
Sodium <i>isovalerate</i> , $N/10$ .....	2520	2350	—
Chloroacetic acid, $N$ .....	2620	2500	0.155
Sodium chloroacetate, $N$ .....	2610	2490	—
Trichloroacetic acid, $N$ .....	2730	2590	121 (?)
Sodium trichloroacetate, $N$ .....	2730	2590	—
Phenylacetic acid, $N/100$ .....	2695	2330	0.0056
Sodium phenylacetate, $N/100$ .....	2700	2330	—

Trichloroacetic acid and its salt were also photographed in more dilute solutions, and their spectra remained identical down to 1 cm. of  $N/100$ -solution.

*The Dibasic Acids.*—In this series, as in the fatty, the change is most marked in the lower members, having almost disappeared in the case of succinic acid. In the neutralisation of  $N$ -oxalic acid, potassium was used instead of sodium, as the oxalate of the latter is not sufficiently soluble; both metals were examined in  $N/10$ -solution, the two spectra being almost identical. Fumaric acid was examined in order to see if the property of simple unsaturation produced any effect; it will be noted that both acid and salt have the same absorptive power. Calcium malonate and calcium succinate were also photographed, the former in  $N/100$ - and the latter in  $N/10$ -solution; it being thought that in these cases the

presence of a bivalent metal might give rise to a cyclic compound. Unfortunately at the dilutions used both salts are practically diactic, so that, even if a ring is formed, it produces no increase in absorptive power, at any rate in aqueous solutions.

It is interesting to note that whilst conjugation of unsaturated centres does not of necessity induce change in absorptive power on salt-formation, still the view put forward in two former papers (Crymble, Stewart, Wright, Rea, and Glendinning, T., 1911, **99**, 541, 1262)—that greater general absorption is shown by compounds possessing such conjugation than by those in which it is absent—finds strong confirmation in the results obtained for this series. Of the first three members oxalic acid shows the greatest absorption, and succinic the least, proving that the effect of conjugation can outweigh that of increasing molecular weight.

TABLE II.

	10 cm. Spectrum transmitted	1 cm. Spectrum transmitted	$\kappa$ .
	to A.	to A.	
Oxalic acid, N .....	2600	2500	10.0 (g)
Potassium oxalate, N .....	2560	2680	—
Malonic acid, N.....	2520	2440	0.163
Sodium malonate, N.....	2485	2385	—
Succinic acid, N.....	2460	2350	0.0066
Sodium succinate, N.....	2400	2340	—
Fumaric acid, N/100.....	3005	2720	0.09
Sodium fumarate, N/100 .....	3600	2720	—

More dilute solutions were examined in the cases of oxalic and fumaric acids, the results being in harmony with those obtained for the higher concentrations.

*Various Aromatic Acids.*—Acids which contain an aromatic nucleus often exhibit a greater change in absorptive power on neutralisation than do those of an aliphatic nature. The indicators, and the "pseudo-acids" of Hantzsch, all possess this property in a marked degree; fundamental difference of structure between the acid and its salt being in these cases the generally accepted explanation. Numerous compounds of a phenolic nature, as investigated by Baly and others (T., 1905, **87**, 1345; 1910, **97**, 1494) also show considerable change on the addition of sodium hydroxide, but the cause of the change is not quite so evident. Finally, there are many acids of an aromatic nature the spectra of which are either identical with those of their sodium salts, or else differ from the latter only in a very slight degree. In this last group we may place benzoic acid, and the homologous compounds, phenyl-

acetic and phenylpropionic acid. The following table contains the results for a few of the more simple compounds photographed in aqueous solutions.

TABLE III.

	10 cm. Spectrum transmitted to A.	1 cm. Spectrum transmitted to A.	$\kappa$ .
Benzoic acid, N/100 .....	2935	2875	0.0060
Sodium benzoate, N/100 .....	2865	2790	—
Phenylacetic acid, N/100 .....	2695	2330	0.0056
Sodium phenylacetate, N/100 .....	2700	2339	—
Phenylpropionic acid, N/100 .....	2710	2310	0.0023
Sodium phenylpropionate, N/100 .....	2710	2300	—
Cinnamic acid, N/1000 .....	3190	3100	0.0035
Sodium cinnamate, N/1000 .....	3090	3005	—
Salicylic acid, N/100 .....	3400	3320	0.162
Sodium salicylate, N/100 .....	3490	3350	—
Phenol, N/10 .....	2920	2875	very small
Sodium phenoxide, N/10 .....	3180	3135	—
Thiolic acid, N/10,000 .....	4350	2320	very great
Sodium thioate, N/10,000 .....	4350	2320	—
Hippuric acid, N/100 .....	2895	2820	0.0222
Sodium hippurate, N/100 .....	2890	2820	—

The absorption bands which exist in phenol and its derivatives have been left out of account in the above table; also, most of the compounds were examined in more dilute solutions, the results being in agreement with those given.

*Inorganic Acids.*—For the most part the inorganic acids are unsuitable for this type of investigation, for since the property of homology is absent, it is not possible to draw comparisons between acids of gradually varying structure; moreover, a considerable number of the inorganic acids and salts are too diastinct to admit of investigation. Mention should be made of the work of Hartley, who has shown that nitric acid and its potassium salt give identical spectra (T., 1902, 81, 556), whilst Ostwald has made a large number of experiments with the permanganates and other coloured salts.

Two cases of interest will be mentioned out of the few acids examined. Hydrogen sulphide and arsenious acid both show a large increase in absorption on neutralisation with sodium hydroxide.

TABLE IV.

	Acid.		Salt.	
	10 cm.	1 cm.	10 cm.	1 cm.
Hydrogen sulphide, N/10 ..	2180	2350	2790	2655
Arsenious acid, M/10 .....	2435	2320	2695	2570

## EXPERIMENTAL.

The water used in this investigation was distilled from silica, the vapour being passed over red-hot silica wool. A sample of 10 cm. thickness was diatropic to  $\lambda=2260$ .

As a rule, the salts were prepared by the addition of excess of sodium hydroxide to the acid. The sodium hydroxide used was prepared from metallic sodium. A 10 cm. length of 2N-solution was diatropic to  $\lambda=2330$ . The substances used were purified so as to give constant melting or boiling points. The hydrogen sulphide was prepared from iron sulphide, and was purified by passing the dry gas over iodine; it was then well washed before being absorbed. The strength of the solution was estimated by means of iron alum and potassium permanganate.

In every case the acid and its salt were photographed on the same plate, thus avoiding errors due to difference of development; moreover, various other thicknesses were examined besides those tabulated.

*Summary.*

Although it is hardly possible with the present data to state definitely when an acid will show an absorption spectrum different from that of its sodium salt; still, the following points seem clear.

1. The change in degree of ionisation which takes place on the neutralisation of an acid does not in itself of necessity produce a change in the absorption spectrum.

2. Many acids show spectra differing from those of their sodium salts, even when the structure of the acid is so simple as to scarcely admit of molecular rearrangement.

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LX.—*Metaphosphoric Acid and its Alkali Salts.*<sup>\*</sup>

By ALFRED HOLT and JAMES ECKERSLEY MYERS.

At least six series of metaphosphates have been described by various investigators. They are supposed to be derived from a corresponding series of acids, but the evidence for their constitution depends either on the method of preparation or empirical composition, for being mainly insoluble substances, little or nothing is known as to their molecular weights.

<sup>\*</sup> For abstract, see P., 1913, 29, 61.

Metaphosphoric acid, obtained either by dehydrating the ortho-acid or by treating phosphoric oxide with moist air, has been found by Tilden and Barnett to possess when in a state of vapour a molecular weight corresponding with the formula  $(\text{HPO}_3)_2$ , and we have already shown (T., 1911, 99, 384) that from freezing-point determinations the ordinary glacial sticks when in solution probably consist of termolecular complexes, whilst the acid obtained by decomposition of lead metaphosphate is present in single molecules. We have also described three varieties of the meta-acid, each characterised by its behaviour towards water. The present communication contains a re-examination of many of these points.

The first series of experiments was directed towards the changes produced by heat on the density and composition of commercial metaphosphoric acid.

Composition, per cent.	Length of heating, in hours.	Density.*	Loss in weight between each heating, per cent.	Total loss in weight, per cent.	Behaviour on solution.
$\left. \begin{array}{l} 74.2 \text{ P}_2\text{O}_5 \\ (83.87 \text{ HPO}_3) \end{array} \right\}$	—	1.214	—	—	Readily soluble
$\left. \begin{array}{l} 77.7 \text{ P}_2\text{O}_5 \\ (89.29 \text{ HPO}_3) \end{array} \right\}$	4	1.350	4.5	4.5	Dissolves easily with crackling
$\left. \begin{array}{l} 78.7 \text{ P}_2\text{O}_5 \\ (89.9 \text{ HPO}_3) \end{array} \right\}$	5½	1.353	6.23	10.78	Soluble with difficulty, crackles
$\left. \begin{array}{l} 78.7 \text{ P}_2\text{O}_5 \\ (89.9 \text{ HPO}_3) \end{array} \right\}$	6½	1.404	7.6	18.38	„ „

\* The values previously given (T., 1911, 99, 390, 391) should be 1.458 and 1.216 instead of 2.488 and 2.216 respectively.

The heating was carried out in a platinum dish over an efficient Meker burner, and it will be seen from the above data that once the glass has attained a composition of about 78 per cent. of phosphoric oxide no great change occurs in the composition of the glass or vapour. The rate of volatilisation of the glass was about 0.1 gram per hour at the temperature of the experiment. This constancy of composition (78.7 per cent. of phosphoric oxide) is lower than is required theoretically for metaphosphoric acid (88.7 per cent.) and is still lower than the value of Tilden and Barnett.

This low percentage of phosphoric oxide could be accounted for by the presence of a small quantity of sodium metaphosphate, a very common impurity in ordinary glacial acid. If a sodium salt, which is not volatile, was present, the percentage of phosphoric oxide in the glass should diminish as the acid was volatilised away, but as 7.6 per cent. of glass can be thus removed with no change in composition, the presence of a sodium salt is improbable. It is

noticeable that this low value for the phosphoric oxide content is nearly that required for pyrophosphoric acid (79.7 per cent.), and hence it might very reasonably be concluded that the heating had been insufficient to do more than form the pyro-acid, and that this, like the meta-variety, is somewhat volatile.

The objections to this view are that the reactions of a solution of this glass in water are not those of pyrophosphoric acid, that it was prepared by heating a substance (glacial acid), which showed the reactions of metaphosphoric acid, and that the precipitate obtained by adding barium chloride to a solution of the glass in water gave a ratio:

$$\frac{\text{Ba precipitate}}{\text{BaSO}_4} = 1.319,$$

the theoretical value for  $\text{Ba}(\text{PO}_3)_2$  being 1.266. These values are in fair agreement, particularly as the determined ratio is too high, for the presence of any other phosphate would lower it.

The freezing points of solutions of these acids in water were also examined, and the results are contained in the annexed table:

Composition of acid, per cent.	Strength of solution in grams per 100 c.c.	Mol. wt. calculated from freezing point.
74.2 $\text{P}_2\text{O}_5$ .....	6.7	198
74.2 $\text{P}_2\text{O}_5$ .....	3.32	185
74.2 $\text{P}_2\text{O}_5$ .....	0.67	138
77.7 $\text{P}_2\text{O}_5$ .....	4.43	123
77.7 $\text{P}_2\text{O}_5$ .....	1.93	156
78.7 $\text{P}_2\text{O}_5$ .....	3.17	170

From these values it is probable that the acid is present in solution as termolecular complexes more or less dissociated. It is true that these values would equally well agree with the molecular weight of pyro-acid (178), but reasons have been given which render the presence of this compound very unlikely.

The acid obtained by decomposing lead metaphosphate gives different results.

The lead salt was prepared by the action of lead acetate solution on a solution of glacial phosphoric acid exactly neutralised by potassium hydroxide, and had the empirical composition  $\text{Pb}(\text{PO}_3)_2$ . It was decomposed with hydrogen sulphide, and a solution containing 3.272 grams of metaphosphoric acid per 100 c.c. was prepared. This gave a freezing point in agreement with a molecular weight of 73.  $\text{HPO}_3$  requires M.W. = 80.

A portion of this solution was then evaporated to dryness, and the resulting glass cautiously heated to redness. After cooling it was dissolved in just so much water as again to yield a solution containing 3.272 grams per 100 c.c. This solution now gave a





Attempts to prepare dimetaphosphates have not been successful. When orthophosphoric acid was heated with the oxides of zinc or copper, and the resulting mass decomposed by the action of an alkaline sulphide, the addition of alcohol precipitated a gelatinous substance which it was found almost impossible to free from the rest of the solution. When filtered and dried as well as possible it was found to contain 43 to 45 per cent. of phosphoric oxide, which is too low a value for any simple alkaline phosphate. The sodium salt prepared from zinc oxide and orthophosphoric acid appeared to have a molecular weight in solution of about 154, whilst that of the corresponding potassium salt from the copper compound was about 339. They are therefore probably mixtures of sodium salts and phosphoric acids, and not definite compounds.

#### *Conclusions.*

1. The hydration of metaphosphoric acid is unimolecular when the acid is present in solution in simple molecules.
2. Alkaline monometaphosphates are soluble in water.
3. The alkaline metaphosphates appear to be derived from mono- and tri-metaphosphoric acid.

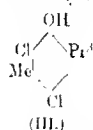
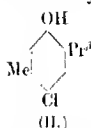
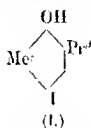
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### *LXI.—The Action of Chlorine on Thymol and on m-Cresol.*

By HORACE LESLIE CROWTHER and HAMILTON MCCOMBIE.

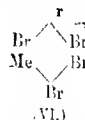
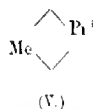
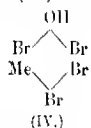
IN continuation of the study of the action of chlorine on iodophenols (Brazier and McCombie, T., 1912, **101**, 968; King and McCombie, T., 1913, **103**, 220), the authors investigated the action of chlorine on 6-iodothymol (I). It was found that this compound, on chlorination in carbon tetrachloride solution, readily lost iodine, and after chlorination for one to two hours, a compound,  $C_{10}H_9OCl$ , was obtained. On chlorination for a further period, a substance was obtained which proved to be a derivative of *m*-cresol. As the iodine was so easily displaced by chlorine from 6-iodothymol (I), the process evidently resolved itself into a chlorination of thymol in the presence of iodine, and, since not only thymol derivatives resulted, but also *m*-cresol compounds, the authors have investigated the action of chlorine on these two substances, under different conditions of temperature, in different solvents, and in the presence of several catalysts.

Very little seems to have been done with regard to the chlorination of thymol. By the action of sulphuryl chloride on thymol, Bocchi (*Gazzetta*, 1897, **26**, ii, 403) and Peratoner and Condorelli (*ibid.*, 1899, **28**, i, 214) were able to prepare 6-chlorothymol (II); the same compound has also been obtained by Robertson and Briscoe (*T.*, 1912, **101**, 1968) by the direct action of the theoretical quantity of chlorine on thymol. Blum (*Zeitsch. physiol. Chem.*, 1893, **16**, 518), by boiling 2:6-dichlorothymolglycuronic acid with sulphuric acid, isolated 2:6-dichlorothymol (III). In a paper entitled "Etudes sur l'essence de thym," Lallemand (*Ann. Chim.*



*Phys.*, 1857, [iii], **49**, 148) describes a trichloro- and a pentachloro-thymol, both of which he obtained by the direct chlorination of thymol. The pentachloro-compound is described as decomposing at 200° with the formation of propylene and tetrachloro-*m*-cresol.

Several benzenoid compounds, containing the *isopropyl* group, on chlorination and bromination, appear to lose that group very easily. Thus Dahner, in a paper on the nitration of bromophenols (*Annalen*, 1901, **333**, 346), found it impossible to introduce more than two atoms of bromine into the thymol molecule, even by acting on it with a large excess of bromine. The product which he obtained, employing excess of bromine, was 2:4:5:6-tetrabromo-*m*-cresol (IV). A similar elimination of the *isopropyl* group was

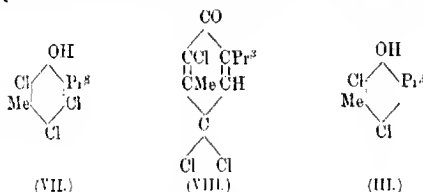


also noticed by Arnand (*Compt. rend.*, 1898, **126**, 1284). This experimenter found that *cymene* (V), on bromination in the presence of aluminium bromide, gave rise to pentabromotoluene (VI), whilst thymol under similar conditions yielded 2:4:5:6-tetrabromo-*m*-cresol (IV).

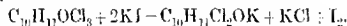
### 1. Direct Chlorination of Thymol.

If solid thymol is subjected to the action of chlorine, it is at once attacked with the evolution of much hydrogen chloride. The thymol is liquefied by the great amount of heat evolved, and the colour of the solution changes to dark red, which gradually lightens

on continued chlorination. Finally, a yellow, crystalline substance is obtained, which is identical with the compound described by Lallemand (*loc. cit.*) as 2:5:6-trichlorothymol (VII). From the fact that this trichloro-compound did not dissolve in sodium hydroxide, but was slowly decomposed by it on warming, and, from the further fact that no acyl derivatives of it could be obtained, it was suspected that this substance was not trichlorothymol, but was 2:4:4-trichloro-3-methyl-6-isopropyl- $\Delta^{2:5}$ -cyclohexadienone (VIII). A further argument for this constitution of the substance is furnished by its behaviour towards potassium iodide. If the compound is treated with potassium iodide in acetic acid solution, iodine is at once liberated, and the reaction can be followed quantitatively by titrating the iodine liberated with  $N/10$ -sodium thiosulphate. It was found that two atoms of iodine were liberated



for every molecule of the trichloro-compound, and the equation representing the transformation is as follows:

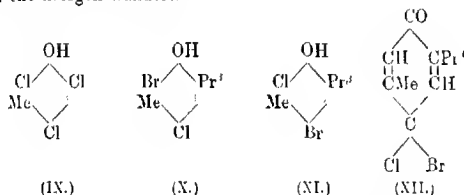


From the potassium salt of the dichlorothymol which is produced in this reaction, the acetic acid forms the free phenol (III), and, when the reaction mixture is poured into water, this compound separates as an oil. This compound is probably identical with the dichlorothymol described by Blum (*loc. cit.*), although the latter gives no boiling point for his compound. In contradistinction to the dichloro-compound, 2:6-dichlorothymol is readily soluble in potassium hydroxide, and, with methyl sulphate, yields a methyl derivative, thus establishing the existence of a hydroxyl group in its molecule. By leading chlorine into the oily 2:6-dichlorothymol, hydrogen chloride is evolved, and the trichlorocyclohexadienone is regenerated.

The so-called trichlorothymol is described, both in Beilstein's "Handbuch," and in Richter's "Lexikon," as forming an isomeric compound on treatment with sulphuric acid at 100°. This appears to be a mistake, for, on referring to Lallemand's original paper, we find the statement made by him is that the trichlorothymol is transformed by the action of sulphuric acid at 100° into "l'acide phénique trichloré." The authors have repeated this reaction, and

have found that the trichloro-compound was very easily decomposed by sulphuric acid at 100°, little or no charring took place, and the resulting compound was 2:4:6-trichloro-*m*-cresol (IX). This compound is dealt with later under the chlorination of *m*-cresol. The melting point of the "isomeric trichlorothymol" mentioned in Beilstein and of Lallemant's "acide phénique trichloré" agrees well with that obtained by the authors for trichloro-*m*-cresol, namely, 46°.

This formation of trichloro-*m*-cresol by the action of sulphuric acid on trichloromethylisopropylcyclohexadienone (VIII) must be brought about by the elimination of the isopropyl group and the migration of one of the chlorine atoms into the position occupied by the isopropyl group. A somewhat similar migration of halogen atoms in the thymol series has been noticed by Robertson and Briscoe (*loc. cit.*), who have shown that 6-chlorothymol (II), on bromination, yields a mixture of 6-chloro-2-bromothymol (X) and 2-chloro-6-bromothymol (XI). To explain this, these authors assume that an intermediate compound (XII) is formed, and that then the halogen wanders.

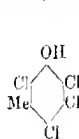


The chlorination of thymol in carbon tetrachloride solution did not proceed very far, for the resulting product was an oil, probably dichlorothymol. From this yellow oil there separated sometimes, after the solution had remained for a long time, a few crystals of the trichloro-compound. Without the presence of a catalyst, the chlorination could, under no conditions, be carried further than the trichloro-compound.

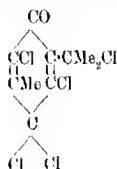
## 2. Chlorination of Thymol in Presence of Iodine.

If thymol is chlorinated for several hours at the ordinary temperature, in dilute carbon tetrachloride or acetic acid solution, the first product that can be isolated is a small quantity of a pentachloro-compound. This product, on gently warming in acetic acid or alcoholic solution, slowly liberated iodine from potassium iodide, but it was found impossible to follow the reaction quantitatively. The pentachloro-compound was insoluble in potassium hydroxide,

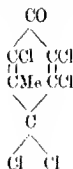
and formed no acetyl or benzoyl derivatives. It was decomposed by concentrated sulphuric acid at 150–200°, with much charring and the formation of a small quantity of tetrachloro-*m*-cresol (XIII). These reactions are analogous to those of the trichloro-compound, and the pentachloro-compound is most probably 2:4:4:5-tetrachloro-3-methyl-6-β-chloroisopropyl-Δ<sup>2:5</sup>-cyclohexadienone (XIV).



(XIII.)



(XIV.)

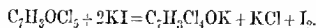


(XV.)

It was found to be almost impossible to arrest the chlorination at the stage of the production of this pentachloro-compound, especially in more concentrated solutions, as the *isopropyl* group was very readily eliminated with the production of *m*-cresol derivatives. The next product which was formed after the pentachloro-compound was 2:4:5:6-tetrachloro-*m*-cresol (XIII), which separated from the concentrated carbon tetrachloride solution. This substance yielded both an acetyl and a benzoyl derivative, thus showing the presence of a hydroxyl group in the molecule; the compound did not liberate iodine from potassium iodide.

Tetrachloro-*m*-cresol is mentioned by Lallemand as being formed by the decomposition of pure pentachlorothymol, but the melting point of it, as given by that experimenter, appears to be very low.

Tetrachloro-*m*-cresol, on chlorination in carbon tetrachloride solution, in the presence of iodine, passed very readily into 2:4:4:5:6-pentachloro-3-methyl-Δ<sup>2:5</sup>-cyclohexadienone (XV), which was found to be the chief and final product of the complete chlorination of thymol in the presence of iodine. The constitution of this compound was established by reactions similar to those employed in the case of 2:4:4-trichloro-3-methyl-6-*isopropyl*-Δ<sup>2:5</sup>-cyclohexadienone (VIII). It liberated iodine very readily from potassium iodide in alcoholic or acetic acid solution, and, by titrating the iodine thus liberated, the reaction was followed quantitatively, and was found to agree with the following equation:



No acetyl or benzoyl derivatives could be obtained from this substance, and the compound was easily attacked and decomposed by alkalis. On treatment with concentrated sulphuric acid at 100°, 2:4:4:5:6-pentachloro-3-methyl-Δ<sup>2:5</sup>-cyclohexadienone was

oxidised very readily to 2:4:5-trichlorotoluquinone (XVI). The identity of this last compound was established by a mixed melting-point determination with a specimen of the trichlorotoluquinone prepared by the oxidation of *o*-toluidine with sodium dichromate (compare Elbs and Brunschweiler, *J. pr. Chem.*, 1896, [ii], 52, 539). Small quantities of 2:4:5-trichlorotoluquinone were also obtained by the prolonged chlorination (lasting for about ten days) of thymol in presence of iodine, in carbon tetrachloride solution.

### 3. Chlorination of Thymol in the Presence of Reduced Iron.

In the hope of obtaining better yields of the pentachloro-derivative from thymol, the chlorination was carried out in the presence of a small quantity of reduced iron. The iron, however, seemed to have a much greater catalytic effect than the iodine. The solution to be chlorinated was a solution of thymol in carbon tetrachloride, a little reduced iron was added, and the mixture was cooled in a freezing mixture. The following results were obtained:

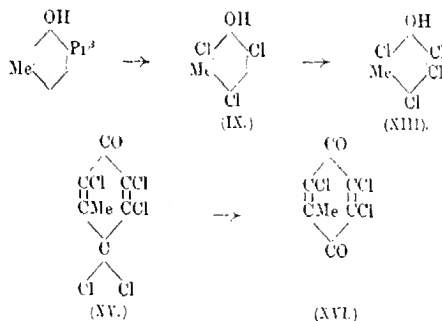
After twenty minutes, an oil.

After three-quarters to one and a half hours, 2:4:6-trichloro-*m*-cresol.

After two to three hours, tetrachloro-*m*-cresol.

After four hours and allowing the solution to remain in presence of the iron overnight, tetrachloro-*m*-cresol and a small quantity of 2:4:5-trichlorotoluquinone.

If the chlorination took place at the ordinary temperature, then, after three to four hours, there resulted pentachloromethylcyclohexadienone (XV).



Thus thymol, on chlorination in the presence of iron, even in an ice-cold solution, decomposed with the formation of trichloro-

*m*-cresol and isopropyl chloride. The trichloro-*m*-cresol was also obtained by the direct chlorination of *m*-cresol, and will be dealt with later. The isopropyl chloride could not be isolated satisfactorily, as it could not be separated from the large excess of carbon tetrachloride, in which solvent the chlorination was conducted. On distillation of the solution a fraction was obtained which seemed to be a mixture of isopropyl chloride and carbon tetrachloride of constant boiling point.

#### 4. Chlorination of Thymol in the Presence of Aluminium-Mercury.

This catalyst has a very similar effect on the chlorination to that exerted by the reduced iron, but the action was not nearly so vigorous as in the case of the latter. The first product which could be isolated in this case was 2:4:6-trichloro-*m*-cresol.

#### 5. Chlorination of *m*-Cresol.

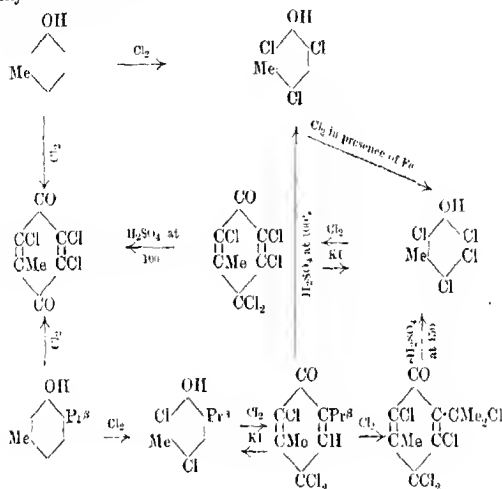
When chlorinated, *m*-cresol passes directly to the 2:4:6-trichloro-compound. The chlorination was carried out under different conditions, namely, (1) in the presence of reduced iron in ice-cold solution; (2) by leading chlorine for six hours into boiling *m*-cresol; and (3) in carbon tetrachloride solution at the ordinary temperature. All these three methods of chlorination gave, as first product, 2:4:6-trichloro-*m*-cresol. The first two methods gave very impure products, which required many recrystallisations before the substance was obtained in a pure state. After evaporating off the solvent, the third method was found to give by far the purest product.

A compound obtained by the direct chlorination of boiling *m*-cresol is described by Claus and Schweitzer (*Ber.*, 1886, **19**, 930) as dichloro-*m*-cresol. These experimenters give the melting point of their compound as 46°, which is identical with that of the trichloro-compound prepared by the authors. Many attempts have been made to prepare a mono- and a dichloro-*m*-cresol by chlorination for different periods of time in carbon tetrachloride solution. These all failed, for the first product which was invariably obtained was trichloro-*m*-cresol. The trichloro-*m*-cresol yields a methyl and an acetyl derivative, and, from analyses of these two compounds and also of the parent phenol, it seems evident that Claus and Schweitzer were mistaken.

Further chlorination of *m*-cresol in presence of a catalyst gave rise simply to the higher chlorination products which have been described earlier in dealing with the chlorination of thymol.

The following diagram shows the products which have been

obtained, under different conditions, by the action of chlorine on thymol and on *m*-cresol.



#### EXPERIMENTAL.

2:4:4-Trichloro-3-methyl-6-isopropyl- $\Delta^{2,3}$ -cyclohexadienone,  
 $\text{C}_{16}\text{H}_{11}\text{OCl}_3$  (VIII).

This compound was prepared by the direct chlorination of thymol without any solvent or catalyst. Under the influence of the chlorine the solid thymol gradually liquefied with a considerable evolution of heat, the liquid became dark brown, and then, on continued chlorination, this colour disappeared. The chlorination was stopped when the weight had increased by about two-thirds. A mass of yellow crystals separated when the liquid was allowed to remain at the ordinary temperature for some hours; the crystals were collected and recrystallised from methyl alcohol, when the substance separated in bright yellow needles, which melted at  $63^\circ$ : 0.2022 gave 0.3418  $\text{AgCl}$ .  $\text{Cl} = 41.81$ .

$\text{C}_{16}\text{H}_{11}\text{OCl}_3$  requires  $\text{Cl} = 42.01$  per cent.

2:4:4-Trichloro-3-methyl-6-isopropyl- $\Delta^{2,3}$ -cyclohexadienone is readily soluble in acetic acid, acetone, ether, chloroform, or light petroleum in the cold, and also in hot alcohol. It is insoluble in potassium or sodium hydroxides, but is decomposed by them slowly



on warming. The substance is also decomposed by concentrated sulphuric acid at  $100^{\circ}$ , with little or no charring, and the formation of 2:4:6-trichloro-*m*-cresol. The trichlorocyclohexadienone readily liberates iodine from a solution of potassium iodide in acetic acid solution, with the formation of 2:6-dichlorothymol. This reaction can be followed quantitatively if the liberated iodine is titrated rapidly in an ice-cold solution with  $N/10$ -sodium thiosulphate. It was found that 0.3957 gram of substance gave 0.4080 gram of iodine; the equation  $C_{10}H_{11}OCl_3 + 2KI = C_{10}H_{11}Cl_2OK + KCl + I_2$  requires 0.3965 gram of iodine.

2:6-Dichlorothymol (III).

This compound was prepared by Blum (*loc. cit.*) by heating 2:6-dichlorothymolglycuronic acid with sulphuric acid.

We obtained it by treating 2:4:6-trichloro-3-methyl-6-isopropyl- $\Delta^{2:5}$ -cyclohexadienone in acetic acid solution with excess of potassium iodide. After allowing the mixture to remain for a few minutes, it was poured into a solution of sodium thiosulphate to remove the iodine, and the yellow oil which separated was extracted with ether, washed, dried over sodium sulphate, and distilled under diminished pressure, when the 2:6-dichlorothymol passed over at  $135^{\circ}/12$  mm. (Found,  $Cl=32.7$ .  $C_{10}H_{12}OCl_2$  requires  $Cl=32.42$  per cent.)

2:6-Dichlorothymol is a pale yellow oil, which is almost colourless when freshly distilled, but gradually darkens on exposure to air and light. It is soluble in most organic solvents and in sodium or potassium hydroxides. It does not liberate iodine from potassium iodide. When 2:6-dichlorothymol was subjected to direct chlorination, hydrogen chloride was evolved, and 2:4:6-trichloro-3-methyl-6-isopropyl- $\Delta^{2:5}$ -cyclohexadienone resulted.

2:6-Dichlorothymol Methyl Ether,  $C_{10}H_{11}Cl_2 \cdot OMe$ .—This derivative was prepared by warming 2:6-dichlorothymol with excess of methyl sulphate, destroying the excess of the latter with sodium carbonate, and pouring the resulting solution into water. The oil which separated was extracted with ether, and washed with dilute potassium hydroxide to remove traces of the unchanged phenol, and then with water. The solution was dried over sodium sulphate, and distilled under diminished pressure, when it passed over at  $129^{\circ}/12$  mm.:

0.1871 gave 0.2316  $AgCl$ .  $Cl=30.55$ .

$C_{11}H_{11}OCl_2$  requires  $Cl=30.47$  per cent.

This methyl derivative is a yellow oil very similar in appearance to 2:6-dichlorothymol. It is soluble in most organic solvents, but is insoluble in sodium hydroxide.

2:4:4:5-Tetrachloro-3-methyl-6- $\beta$ -chloroisopropyl- $\Delta^{2:5}$  cyclohexadienone,  $C_{10}H_5OCl_5$  (XIV).

This compound could be prepared only in small quantities by the chlorination, for several hours at the ordinary temperature, of thymol in the presence of iodine, in dilute carbon tetrachloride or acetic acid solutions. The solvent was removed by evaporation, and from the residue, after it had remained for several days, there separated out a few crystals of the cyclohexadienone. The product was crystallised from light petroleum, methyl alcohol, or acetic acid, when it separated in white, flat needles, which melted at  $95^\circ$ :

0.1598 gave 0.3548 AgCl. Cl=54.93.

$C_{10}H_5OCl_5$  requires Cl=55.04 per cent.

This compound formed no acetyl or benzoyl derivatives, and was insoluble in sodium or potassium hydroxides, being slowly decomposed by them on warming. On heating the substance in alcoholic solution it liberated iodine from potassium iodide. The compound was decomposed with much charring by concentrated sulphuric acid at  $150^\circ$ , with the formation of tetrachloro-*m*-cresol, which separated as a solid from the hot acid.

2:4:6-Trichloro-*m*-cresol,  $C_7H_5OCl_3$  (IX).

This substance was prepared by the chlorination, in the presence of iron for about one to two hours, of 3—4 grams of thymol in carbon tetrachloride solution. The solution was cooled in ice, and after evaporating off the solvent a white mass was obtained, which required to be recrystallised five or six times from dilute acetic acid or light petroleum before it was obtained pure. It can also be prepared by the chlorination for several hours of boiling *m*-cresol, and also by the chlorination of *m*-cresol in carbon tetrachloride solution. This last method yields by far the best product. Another method for its preparation is the action of concentrated sulphuric acid at  $100^\circ$  on 2:4:4-trichloro-3-methyl-6- $\beta$ -isopropyl- $\Delta^{2:5}$  cyclohexadienone. The substance, after several recrystallisations, melted at  $46^\circ$ :

0.1924 gave 0.3921 AgCl. Cl=50.42.

$C_7H_5OCl_3$  requires Cl=50.35 per cent.

2:4:6-Trichloro-*m*-cresol is extremely soluble in all the ordinary organic solvents except light petroleum, it is sparingly soluble in boiling water, and readily so in sodium or potassium hydroxides. It has no action on potassium iodide, has a very penetrating odour, and is easily volatile in steam.

2:4:6-Trichloro-*m*-tolyl Methyl Ether,  $C_7H_4Cl_3\cdot OMe$ .—This com-

pound was prepared by warming trichloro-*m*-cresol with excess of methyl sulphate. The excess of the latter was removed with sodium carbonate, and the solid methyl derivative was separated and crystallised from dilute acetic acid, when it separated in small, slender, white needles, which melted at 54--55°:

0.1974 gave 0.3792 AgCl. Cl=47.52.

$C_8H_7OCl_3$  requires Cl=47.23 per cent.

*Acetyl Derivative*,  $C_8H_7Cl_3 \cdot OAc$ .—This derivative was prepared by the action of acetic anhydride on trichloro-*m*-cresol in the presence of a drop of concentrated sulphuric acid. The mixture was poured into water, and the oil which separated was extracted with ether, washed with dilute potassium hydroxide and with water, and allowed to solidify in a vacuum desiccator. The crystals were separated and purified by a second extraction with ether, when they melted at 32°:

0.2031 gave 0.3435 AgCl. Cl=41.84.

$C_8H_7O_2Cl_3$  requires Cl=42.01 per cent.

#### 2:4:5:6-Tetrachloro-*m*-cresol, $C_8H_4OCl_4$ (XIII).

This compound was obtained by the more or less prolonged chlorination of thymol in presence of iodine in a concentrated carbon tetrachloride solution. If iron were used as the catalyst, 3 grams of thymol were converted into tetrachloro-*m*-cresol after chlorination for two to three hours even in an ice cold solution. The tetrachlorocresol separated out from a concentrated solution as a crystalline mass, and, at this point, the chlorination was arrested as the tetrachlorocresol was very easily chlorinated further.

The best method, however, for the preparation of tetrachloro-*m*-cresol consists in treating 2:4:4:5:6-pentachloro-3-methyl- $\Delta^{2:5}$ -cyclohexadienone (the final product of the chlorination of thymol or of *m*-cresol) with excess of potassium iodide, the reaction being carried out in alcoholic or acetic acid solutions. The mixture is poured into sodium thiosulphate solution, and the yield is practically theoretical.

As described previously, tetrachloro-*m*-cresol is also formed by treating 2:4:4:5-tetrachloro-3-methyl-6- $\beta$ -chloroisopropyl- $\Delta^{2:5}$ -cyclohexadienone with sulphuric acid at 150°.

When crystallised from light petroleum, acetic acid, or dilute alcohol, tetrachloro-*m*-cresol separates in slender, white, long needles, which melt at 189--190°:

0.1732 gave 0.4048 AgCl. Cl=57.84.

$C_8H_4OCl_4$  requires Cl=57.73 per cent.

2:4:5:6-Tetrachloro-*m*-cresol is soluble in most organic solvents,

and dissolves in potassium hydroxide, but is unattacked by warm concentrated sulphuric acid. It can be converted easily into acetyl and benzoyl derivatives, and, when treated with chlorine in carbon tetrachloride solution, it yields 2:4:4:5:6-pentachloro-3-methyl- $\Delta^2:5$ -cyclohexadienone.

*Acetyl Derivative*,  $C_7H_5Cl_4OAc$ .—This compound was prepared by the action of acetic anhydride on tetrachloro-*m*-cresol in the presence of a drop of sulphuric acid. On crystallisation from glacial acetic acid it separated in flat needles, which melted at  $117^\circ$ :

0.1955 gave 0.3877 AgCl. Cl=49.07.

$C_7H_5O_2Cl_4$  requires Cl=49.30 per cent.

This compound is insoluble in cold alcohol, but is soluble in cold acetone or ether. It is readily hydrolysed by alcoholic potassium hydroxide.

*Benzoyl Derivative*,  $C_7H_5Cl_4OBz$ .—This derivative was prepared in pyridine solution, and, when crystallised from glacial acetic acid or alcohol, melted at  $143$ — $144^\circ$ :

0.1998 gave 0.3278 AgCl. Cl=40.59.

$C_{14}H_5O_2Cl_4$  requires Cl=40.57 per cent.

2:4:4:5:6-Pentachloro-3-methyl- $\Delta^2:5$ -cyclohexadienone,  
 $C_7H_5OCl_5$  (XV).

This compound was found to be the chief and final product of the complete chlorination of thymol in presence of either iodine or iron. The thymol was dissolved in a small quantity of carbon tetrachloride, a little iron or iodine was added, and a stream of dry chlorine was passed through the solution until the evolution of hydrogen chloride had ceased. In the case of iodine as the catalyst, 5 grams of thymol required chlorination during two days at  $60^\circ$  before the process was complete. With iron, however, the same quantity of thymol required only about four to five hours' chlorination at the ordinary temperature. The pentachlorohexadienone, when crystallised from light petroleum, glacial acetic acid, or alcohol, separated in large, rhombic prisms with a slight yellowish-green tinge, which melted at  $92^\circ$ :

0.1386 gave 0.3528 AgCl. Cl=62.96.

$C_7H_5OCl_5$  requires Cl=63.28 per cent.

2:4:4:5:6-Pentachloro-3-methyl  $\Delta^2:5$ -cyclohexadienone is readily soluble in acetone, benzene, toluene, chloroform, or ether in the cold, but it is insoluble in water. No acetyl or benzoyl derivatives of it could be obtained, and it is insoluble in alkalis. It liberates iodine from potassium iodide in alcoholic or acetic acid solutions, and this reaction was followed quantitatively with the following

result: 0.4650 gram of substance yielded 0.4215 gram of iodine. The equation  $C_7H_3OCl_5 + 2KI = C_7H_3Cl_5OK + KCl + I_2$  requires 0.4210 gram of iodine.

Concentrated sulphuric acid at  $100^\circ$  oxidises the compound very readily to 2:4:5-trichlorotoluquinone, which separates from the hot acid as a yellow, crystalline mass.

2:4:5-Trichlorotoluquinone,  $C_7H_3O_2Cl_3$  (XVI).

This compound was obtained in small quantities, together with tetrachloro-*m*-eresol and 2:4:4:5:6-pentachloro-3-methyl- $\Delta^{2:5}$ -cyclohexadienone, by the prolonged chlorination of thymol in the presence of iodine or reduced iron. In the presence of iodine the chlorination required about ten days, but with reduced iron small quantities of the toluquinone were obtained after chlorination for twelve hours.

The best method of preparation consists in treating 2:4:4:5:6-pentachloro-3-methyl- $\Delta^{2:5}$ -cyclohexadienone with concentrated sulphuric acid at  $100^\circ$ . After a few minutes a yellow, crystalline mass separates, and the reaction is found to be practically quantitative. The substance was recrystallised from a mixture of alcohol and benzene, and melted and decomposed at  $238^\circ$ :

0.1769 gave 0.3368 AgCl.  $Cl = 47.10$ .

$C_7H_3O_2Cl_3$  requires  $Cl = 47.23$  per cent.

The identity of this substance was established by a mixed melting-point determination with a specimen of trichlorotoluquinone prepared by the oxidation of *o*-toluidine with sodium dichromate.

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## LXII.—*The Constituents of the Oil of Cydnus indicus.*

By EDWIN ROY WATSON.

*Cydnus indicus* (Westw.) is an insect which is well known in many parts of India. In Bengal it is attracted to lights, often in large numbers, in the nights of June and the following rainy months. It is notorious on account of its strong and unpleasant odour, which is so strong that one insect is sufficient to scent a whole room. In the vernacular it is known as *gandi*. It is also known as the

*geranium-bug*. The last name perhaps indicates a supposed similarity of the odour to that of the geranium.

The insect is one of the Heteroptera. Maxwell-Lefroy (*Indian Insect Life*) remarks that "a feature of the great majority of the Heteroptera is the aromatic odour they protect themselves with. This odour is due to the secretion by special glands of an oily fluid, which is excreted at will from the odoriferous orifices and rapidly volatilises."

The insects used for this investigation\* were collected in Dacca (E. Bengal) in June. Altogether 453 grams [1 lb.] of material were collected, and estimated to consist of 100,000 insects. They contain a large quantity of oil, and this, after extraction, was found to possess the characteristic and disagreeable odour. A preliminary examination showed that it was mainly a fixed oil of the same general character as other animal oils. It was then found that if the insects were crushed and distilled in a current of steam a small quantity of an oily substance passed over and collected as a lighter layer above the condensed water, and had the characteristic odour, highly concentrated. Ultimately the best yield was obtained by extracting the insects with ether, distilling off the ether on the water-bath, and subjecting the oil to steam distillation. It was thus separated into two parts, namely, (A) a volatile oil, and (B) a non-volatile oil.

The volatile portion was redistilled with steam for further purification. One hundred grams of the insects gave about 1.5 grams of redistilled volatile oil and about 70 grams of the non-volatile oil.

(A) *The Volatile Oil*.—This was separated from the steam distillate by shaking with ether. The ethereal solution was dried, and the ether allowed to evaporate at the ordinary temperature over soda-lime:

0.1193 gave 0.1131  $H_2O$  and 0.3021  $CO_2$ .  $C = 69.07$ ;  $H = 10.34$ .

$C_9H_{16}O_2$  requires  $C = 69.2$ ;  $H = 10.3$  per cent.

This result was not in accordance with the anticipation that this strongly-smelling oil would prove to be a terpene or terpene-alcohol, aldehyde, or ketone. From the high percentage of oxygen it seemed probable that it was a carboxylic acid, or contained a good deal of such an acid substance; and this conjecture was borne out by experiment, for on shaking the oil with dilute aqueous sodium carbonate the greater part of it (about 90 per cent.) passed into solution. The undissolved non-acidic portion was recovered by extraction with ether, drying, and freeing from ether as before.

The alkaline solution was acidified with dilute sulphuric acid.

\* A sample was identified by Dr. N. Annandale of the Indian Museum, not as *Cydnus indicus*, but as the closely-related species *Stibaropus indicus*, Scholtz.

when the acid portion of the oil was liberated. It was likewise extracted with ether, dried, and freed from ether.

*The Acidic Portion of the Volatile Oil.*—Examination showed this to consist of a single substance of the empirical formula  $C_8H_{14}O_2$ , probably *cycloheptanecarboxylic acid*. (Found,  $C=67.49$ ;  $H=10.12$ ; M.W. (by titration with alkali), 141. Calc.,  $C=67.60$ ;  $H=9.86$  per cent.; M.W.=142.)

The exactly neutral solution obtained by the titration of the acid was treated with a solution of calcium chloride and, on keeping, gave a deposit of uniform prismatic crystals of a calcium salt. Further crops of the same crystalline character were obtained by concentrating the solution and allowing to cool. Care was necessary not to carry the concentration too far, or else the calcium salt was deposited from the hot solution, first as a skin on the surface, and then as a semi-solid mass, which solidified on cooling. (Found,  $H_2O=5.1$ .  $(C_8H_{13}O_2)_2Ca \cdot H_2O$  requires  $H_2O=5.3$  per cent. Found,\*  $C=58.05$  †;  $H=8.22$ ;  $CaO=17.61$ .  $(C_8H_{13}O_2)_2Ca$  requires  $C=59.64$ ;  $H=8.08$ ;  $CaO=17.39$  per cent.)

The exact agreement of the analytical figures for the oil with the formula  $C_8H_{14}O_2$ , that of the acid corresponding with the calcium salt which was obtained in pure condition, shows that the oil is a single substance. It boils at  $251^\circ$ , has a strongly acid reaction towards litmus, and shows no tendency to absorb halogen. The acid has a strong, rancid odour, and thus appears to be *cycloheptanecarboxylic acid*.

*Non-acidic Portion of the Volatile Oil.*—The quantity of this substance obtained was only sufficient for ultimate analysis:

0.0970 gave 0.2552  $CO_2$  and 0.0932  $H_2O$ .  $C=71.74$ ;  $H=10.68$ .

$C_{11}H_{20}O_2$  requires  $C=71.73$ ;  $H=10.86$  per cent.

It would not be safe to draw any conclusions as to the constitution of the substance from this analysis alone. It may, however, be remarked that the figures are opposed to the idea that the substance is a terpene, terpene-alcohol, aldehyde, or ketone. This portion of the oil had an odour quite different from that of the acid. To the author it resembled the odour of lemon or geranium, but to others this resemblance was not obvious, and by them it was thought to have the original odour of the insects in a highly concentrated form.

(B) *The Non-volatile Oil.*—The analytical figures obtained show this to be very similar to other animal oils, and as it does not

\* In salt dried at  $140^\circ$ .

† The Ca salt was mixed with potassium dichromate in the combustion boat, but this does not appear to have been sufficient to effect the liberation of the whole of the carbon.

contribute appreciably to the odour of the insect it possesses no special interest.

D <sub>15</sub> <sup>20</sup> .....	0.9135
Free acid (calculated as stearic acid) .....	6.6 per cent.
Insoluble fatty acids (obtained on saponification) .....	94.8 " "
Volatile fatty acids (reckoned as butyric acid) .....	0.6 " "
Potassium hydroxide required for saponification .....	19.1 " "
Iodine absorption .....	49.1 " "

This examination showed that the non-volatile oil did not contain the glyceride of *cycloheptanecarboxylic acid*.

#### Conclusion.

The strong and disagreeable odour of *Cydnaus indicus* is due to *cycloheptanecarboxylic acid* which is present in the insects to the amount of 1½ per cent., and another substance (C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>?) or mixture of substances, present in much smaller quantity (0.1–0.2 per cent.), which has a still stronger odour. The intensity of the odour of the latter substance can be judged from the fact that each insect contains only 0.000005 gram of it, and yet one insect is sufficient to scent a whole room.

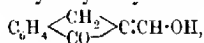
More material will be obtained in June, 1913, and the investigation of this substance continued.

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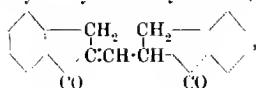
### LXIII.—*Studies on Cyclic Ketones. Part III.*

By SIEGFRIED RHEMANN and STANLEY ISAAC LEVY.

IN Part II. of the present work (T., 1912, 101, 2542) it was shown that the behaviour of 2-hydroxymethylene-1-hydrindene,

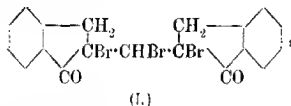


and its methylenedioxy-derivative differs from that of hydroxy-methylenecamphor and other hydroxymethylene compounds, inasmuch as the former are not stable towards heat; thus at the melting point they condense, with the loss of one molecule of formic acid from two molecules of the hydroxymethylene derivative, to the coloured ketohydrindylmethyleneketohydrindene,





and the corresponding methylenedioxy derivative respectively. The constitution of these substances, which, as previously stated (*loc. cit.*), follows from the syntheses and from the formation of salts with alkalis, is supported by their behaviour towards bromine. The condensation product from hydroxymethylenehydrindone yields the colourless tribromo-compound,  $C_{19}H_{13}O_2Br_3$ . Besides the addition of bromine at the ethylene linking, therefore, it follows that substitution of one hydrogen atom by the halogen also occurs. The fact that the total halogen is readily removed by potassium hydroxide points to the formula:



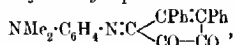
for the bromo-compound.

The remarkable transformation which these hydroxymethylene compounds undergo on heating induced us to prepare analogous derivatives from other cyclic ketones. Having found (*loc. cit.*) that neither 1:3-dimethyl-6-hydroxymethylene-2<sup>3</sup>-cyclohexen-5-one nor 3-methyl-5-hydroxymethylenecyclopentan-1-one\* undergoes any change on heating, we endeavoured to prepare the hydroxymethylene derivative of 2-hydrindone, in the hope that it would behave similarly to the corresponding derivative of 1-hydrindone. It was found, however, that this compound cannot be obtained by the usual method, the hydrindone being transformed into a viscous product. Various attempts to prepare the hydroxymethylene derivative of diphenylcyclopentenone,  $\begin{matrix} \text{CPh}\cdot\text{CH}_2 \\ | \\ \text{CPh}\cdot\text{CH}_2 \end{matrix} > \text{CO}$ , were equally unsuccessful; we could obtain only a very small quantity of a yellow substance, which, although giving in alcoholic solution a strong coloration with ferric chloride, was found to be a mixture.

This unexpected result induced us to subject this cyclic ketone to a closer study, with the view of ascertaining whether it condenses with ethyl oxalate and aromatic aldehydes, and whether the action occurs between one molecule of the ketone and two molecules of these reagent. The investigation appeared to us of interest, also, for another reason. Some time ago (Ruhemann and Naunton, T., 1912, 101, 42) it was shown that the azomethines which are produced by the action of *p*-nitrosodimethylaniline on diphenylcyclopentenone, yield, on treatment with mineral acids, 5-*p*-dimethyl-

\* The authors regret to have overlooked the fact that 3-methyl-5-hydroxymethylenecyclopentan-1-one, which they described in Part II, was obtained before by Wallach (*Annalen*, 1903, 329, 109).

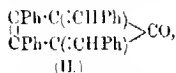
aminoanilo 3:4-diphenyl- $\Delta^{3:4}$ -cyclopentene-1:2-dione,



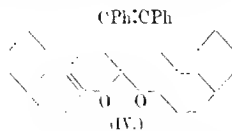
which is characterised by the ease with which its solutions are transformed into the colloidal state (see also Hardy, *Proc. Roy. Soc.*, 1912, A, **87**, 29); and it was in the hope that the further study of diphenylcyclopentenone might bring to light other derivatives of the ketone which possess properties similar to those of the azomethine, that we undertook this work.

It was to be expected that the cyclic ketone would condense with ethyl oxalate to form ethyl diphenylcyclopentenonedioxalate, but this compound could not be obtained, only one molecule of the ester taking part in the reaction to yield *ethyl 3:4-diphenyl- $\Delta^{3:4}$ -cyclopentenone-2-oxalate*,  $\text{CO}_2\text{Et} \cdot \text{CO} \cdot \text{CH} \begin{array}{l} \text{CPh:CPh} \\ \text{CO-CH}_2 \end{array}$ . The yield is unsatisfactory, the larger part of the ketone remaining unaltered. The ester decomposes readily when warmed with dilute potassium hydroxide to the original ketone and potassium oxalate, although if the reaction mixture is allowed to remain for a day without heating, the *acid*,  $\text{CO}_2\text{H} \cdot \text{CO} \cdot \text{CH} \begin{array}{l} \text{CPh:CPh} \\ \text{CO-CH}_2 \end{array}$ , is obtained on the addition of dilute mineral acids.

On the other hand, diphenylcyclopentenone readily condenses with two molecules of aromatic aldehydes when the solution of the mixture in alcohol or glacial acetic acid is saturated with hydrogen chloride. With benzaldehyde, 3:4-diphenyl-2:5-dibenzylidene- $\Delta^{3:4}$ -cyclopentenone,



is formed; similar compounds have been obtained by the action of *p*-nitrobenzaldehyde and of cinnamaldehyde on the ketone. The behaviour of salicylaldehyde is of special interest; as in the above cases, the ketone condenses with two molecules of the aldehyde, but the disalicylidene derivative which is undoubtedly first formed loses a further molecule of water, yielding the yellow pentacyclic anhydride, 3:3'-diphenylacetylenedibenzospirogran (III). Similar com-

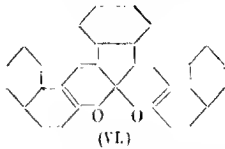
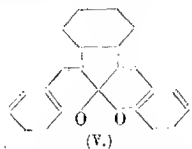


pounds have recently been obtained by Borsche and Geyer

(*Annalen*, 1912, **393**, 29) from saturated alicyclic ketones; we adopt here the system of nomenclature which these authors have given.

In the same way, 2-naphthol-1-aldehyde reacts with diphenylcyclopentenone, forming the yellowish-brown heptacyclic compound, *diphenylacetylenedi-β-naphthaspiropyran* (IV).

As was to be expected, 2-hydrindone reacts with salicylaldehyde as well as with 2-naphthol-1-aldehyde, to yield the hexa- and octacyclic *spiropyran* compounds, *phenylenedibenzospiropyran* (V) and



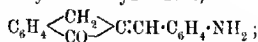
*phenylenedi-β-naphthaspiropyran* (VI), which are red and bluish-black respectively. These cyclic compounds, with the exception of (VI), are characterised by the deep green fluorescence of their solutions in cold concentrated sulphuric acid; in the case of the latter substance, the fluorescence develops only after boiling, and in no case is it apparent in solutions of these substances in other solvents.

None of the above-mentioned condensation products of diphenylcyclopentenone has the property of the azomethine,  $C_{25}H_{20}O_2N_2$ , of being transformed in solution into the colloidal state. This result induced us to examine whether this phenomenon occurs in the case of the corresponding 5-*p*-diethylaminoanilo-3:4-diphenyl-Δ<sup>3:4</sup>-cyclopentene-1:2-dione,  $NEt_2 \cdot C_6H_4 \cdot N : C \begin{smallmatrix} \text{CPh:CPh} \\ \text{CO-CO} \end{smallmatrix}$ . This substance is

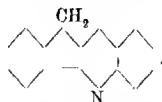
obtained by a method similar to that employed in the case of the dimethyl derivative, namely, by treating the product of the action of *p*-nitrosodiethylaniline on diphenylcyclopentenone with hydrochloric acid. We were surprised to find that the solutions of this compound do not pass into the colloidal state; it seems, therefore, that this behaviour is peculiar to the particular azomethine,  $C_{25}H_{20}O_2N_2$ , since, as previously stated (*loc. cit.*), it is not observed either with the bromo- or nitro-substitution products of this compound.

Since aromatic *o*-hydroxy-aldehydes condense with diphenylcyclopentenone and 2-hydrindone to form *spiropyran* compounds, it occurred to us that aromatic *α*-amino-aldehydes might react with these ketones in a similar manner, to yield *spiro*-compounds containing nitrogen. We are at present engaged in the study of this reaction. In the meantime, we have investigated the behaviour of

*o*-aminobenzaldehyde towards 1-hydrindone, and find that, under the influence of potassium hydroxide, condensation occurs to the orange 2-*o*-aminobenzylidene-1-hydrindone,



under the conditions of the reaction, this substance partly condenses, with loss of one molecule of water, to the colourless indenoquinoline,



The change is complete on boiling the aminobenzylidenehydrindone with hydrochloric acid, when the unstable hydrochloride of the quinoline is formed; this dissociates, on boiling with water, into hydrochloric acid and the free base.

Indenoquinoline has been described by Noelting and Blum (*Ber.*, 1901, **34**, 2467), who obtained it from ketoindenoquinoline, the product of the interaction of *o*-aminobenzaldehyde and 1:3-diketohydrindene, by distillation with zinc dust. These authors give the names quinolylenephenylenemethane and quinolyene phenylene ketone respectively to these compounds, but it appears to us to be more convenient to use the above names, which correspond with the nomenclature generally adopted for polycyclic systems.

#### EXPERIMENTAL.

##### *Action of Bromine on Ketohydrindylmethyleneketohydrindene.*

This reaction takes place on gradually adding bromine to the red condensation product of 2-hydroxymethylene-1-hydrindone, suspended in glacial acetic acid. The halogen is absorbed, and at the same time the solid dissolves, forming a red solution. The clear liquid is kept overnight, and then treated with water, which precipitates a white solid, very sparingly soluble in light petroleum and alcohol, but dissolving readily in boiling benzene. The hot benzene solution is treated with light petroleum (b. p. 60–70°) until it becomes turbid; on cooling, the solid separates in colourless needles, which melt and decompose at 156°:

0.1903 gave 0.3095  $\text{CO}_2$  and 0.0511  $\text{H}_2\text{O}$ .  $\text{C} = 44.36$ ;  $\text{H} = 2.98$ .

0.2580 „ 0.2822  $\text{AgBr}$ .  $\text{Br} = 46.53$ .

$\text{C}_{19}\text{H}_{12}\text{O}_2\text{Br}_2$  requires  $\text{C} = 44.44$ ;  $\text{H} = 2.53$ ;  $\text{Br} = 46.78$  per cent.

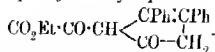
The *dibromide* of ketohydrindylmethyleneketobromohydrindene (1) readily loses its whole content of bromine on the addition of alcoholic potassium hydroxide to the hot alcoholic solution. The

mixture develops a deep red coloration, which at first rapidly disappears, remaining permanent only when a slight excess over the required amount (3 molecules) of the alkali has been added. On concentration, the solution deposits a faintly yellow solid, which is insoluble in water, but dissolves, although not readily, in potassium hydroxide to yield a red solution. Qualitative tests show that it contains no bromine, but as yet the nature of the compound has not been further studied.

*Action of Ethyl Formate on 3:4-Diphenylcyclopentenone.*

The cyclopentenone required for this work was prepared, as previously (T., 1912, **101**, 42), according to the directions of Japp and Lander (T., 1897, **71**, 131). It was found, however, that the yield of the pure compound is considerably greater than, indeed, more than twice as great as that given by these authors. With the object of preparing the hydroxymethylene derivative of the cyclopentenone and studying its behaviour, the ketone (4.6 grams) was dissolved in absolute ether (of which a large volume is required, owing to the sparing solubility in this solvent), and mixed with ethyl formate (3.1 grams, two molecules); on gradually adding the solution to sodium ethoxide (2.7 grams, two molecules) suspended in ether, the whole being maintained at 0°, a deep red coloration was immediately developed, and a small quantity of a dark solid separated, which, however, did not perceptibly increase on keeping. After three days the whole was shaken with ice-water, and the aqueous layer, after being freed from ether by means of a current of air, was acidified with acetic acid. A very small quantity of a yellow solid was precipitated, but although the alcoholic solution gave a green coloration with ferric chloride, the product proved to be a mixture from which no pure substance could be separated.

An attempt to carry out the condensation, using quantities corresponding with one molecule each of ketone, ester, and sodium ethoxide, was even less successful; on acidifying the aqueous layer obtained from the reaction mixture only a slight opalescence was observed. Finally, the ketone was heated with excess of ethyl formate to 150° in a sealed tube for an hour, in the hope that the hydroxymethylene derivative which might be formed would condense to a coloured compound analogous to that obtained from 2-hydroxymethylene-1-hydrindone; on opening the tube, however, the reagents were found to have remained unchanged.

*Ethyl 3:4-Diphenyl-Δ<sup>3:4</sup>-cyclopentenone-2-oxalate,*

This ester is formed, in place of the ethyl diphenylcyclopentenone-dioxalate, which might have been expected, when the *cyclopentenone* is treated with two equivalents of sodium ethoxide and ethyl oxalate. On adding the mixture of the ketone (4.7 grams) and ethyl oxalate (6.0 grams), dissolved in absolute ether, to sodium ethoxide (2.8 grams) suspended in ether, the liquid darkens, and deposits a brown solid, which gradually increases in quantity. After keeping for four days, the solid is collected and treated with dilute sulphuric acid, and the whole extracted with ether. The yellow substance left on evaporation of the ethereal solution, is readily soluble in hot dilute alcohol, from which it crystallises on cooling in light yellow needles melting at 131–132°. The alcoholic solution gives a reddish-brown coloration with ferric chloride:

0.2039 gave 0.5652 CO<sub>2</sub> and 0.0985 H<sub>2</sub>O. C = 75.60; H = 5.36.

C<sub>21</sub>H<sub>15</sub>O<sub>4</sub> requires C = 75.45; H = 5.39 per cent.

*Ethyl 3:4-diphenyl-Δ<sup>3:4</sup>-cyclopentenone-2-oxalate* readily dissolves in dilute potassium hydroxide; on heating for a short time, the solution deposits a solid which was identified with the *cyclopentenone*, and the alkaline liquid then contains oxalic acid. Under these conditions, therefore, the ester decomposes. Hydrolysis to the acid, however, can be effected by the action of dilute potassium hydroxide at the ordinary temperature. On keeping the alkaline solution overnight, and then adding dilute hydrochloric acid, 3:4-diphenyl-Δ<sup>3:4</sup>-cyclopentenone-2-oxalic acid separates as a deep yellow solid, which crystallises from hot dilute alcohol in long needles; the alcoholic solution gives a reddish-brown coloration with ferric chloride. The substance melts gradually at 175–183°, this behaviour being probably due to the presence of a small quantity of unchanged ester:

0.2076 gave 0.5675 CO<sub>2</sub> and 0.0923 H<sub>2</sub>O. C = 74.55; H = 4.94.

C<sub>19</sub>H<sub>13</sub>O<sub>4</sub> requires C = 74.51; H = 4.58 per cent.

*Action of Aromatic Aldehydes on Diphenylcyclopentenone.**3:4-Diphenyl-2:5-dibenzylidene-Δ<sup>3:4</sup>-cyclopentenone (II).*

Benzaldehyde does not condense with the *cyclopentenone* under the influence of heat, even when the mixture is kept at 180°. An action occurs, however, on adding alcoholic potassium hydroxide to the mixture of aldehyde and ketone, dissolved in alcohol, at the ordinary temperature, but the quantity of solid which separates is

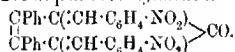
quite inconsiderable, even after several days. The condensation takes place much more readily when hydrogen chloride is used, instead of the alkali. The solution of the ketone (3 grams) and the aldehyde (2.7 grams) in glacial acetic acid, after saturation with the gas at 0°, develops a deep red coloration, and in the course of three days the whole sets to a semi-solid mass of red crystals. The product is almost insoluble in cold alcohol, but dissolves sparingly in the boiling solvent; on cooling, it crystallises in orange needles, which turn red and soften at about 190°, and melt at 201–202°:

0.2080 gave 0.6915 CO<sub>2</sub> and 0.1005 H<sub>2</sub>O. C=90.67; H=5.37.

C<sub>31</sub>H<sub>22</sub>O requires C=90.73; H=5.37 per cent.

The substance dissolves gradually in cold concentrated sulphuric acid, forming a yellowish-brown solution, which gradually deepens in colour.

3:4-Diphenyl-2:5-di-*p*-nitrobenzylidene-Δ<sup>3:4</sup>-cyclopentenone,



*p*-Nitrobenzaldehyde condenses with the cyclopentenone when the solution of the two compounds in alcohol or glacial acetic acid is saturated with hydrogen chloride at 0°; the reaction is complete after keeping the mixture for a week. The red solid which separates is insoluble in alcohol, and only sparingly soluble in boiling glacial acetic acid. After washing with hot alcohol and drying in the steam-oven it melts and decomposes at about 308°:

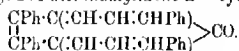
0.1982 gave 0.5415 CO<sub>2</sub> and 0.0728 H<sub>2</sub>O. C=74.51; H=4.08.

0.2375 „ 12.0 c.c. N<sub>2</sub> at 20° and 746 mm. N=5.67.

C<sub>31</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub> requires C=74.40; H=4.00; N=5.60 per cent.

With cold concentrated sulphuric acid the compound dissolves to a brownish-green solution, which darkens considerably in colour after a short time.

3:4-Diphenyl-2:5-dicinnamylidene-Δ<sup>3:4</sup>-cyclopentenone,



This compound, like the above, is readily obtained by the use of hydrogen chloride as a condensing agent. On passing the gas into the cooled mixture of the aldehyde (3.4 grams) and the ketone (3 grams) dissolved in glacial acetic acid, a deep red coloration develops, and after a day, the whole sets to a semi-solid mass of crystals. The product is insoluble in cold, sparingly soluble in hot alcohol; it dissolves in much boiling glacial acetic acid, separating

on cooling in scarlet needles, which soften at about  $225^{\circ}$  and melt at  $234^{\circ}$ :

0.2124 gave 0.7080  $\text{CO}_2$  and 0.1082  $\text{H}_2\text{O}$ .  $\text{C}=90.90$ ;  $\text{H}=5.66$ .

$\text{C}_{35}\text{H}_{35}\text{O}$  requires  $\text{C}=90.91$ ;  $\text{H}=5.63$  per cent.

The substance dissolves in cold concentrated sulphuric acid to a deep blue solution, which after a short time becomes reddish-violet, and finally red.

When alcoholic potassium hydroxide is employed in place of hydrogen chloride as a condensing agent, a viscous product is obtained; in the course of a day, this sets to a brittle, red solid, from which no crystalline substance could be isolated.

*The Anhydride of 3:4-Diphenyl-2:5-disalicylidene-3<sup>5</sup>:4-cyclopentenone (3:3'-Diphenylacetylenedibenzospiropyran), (III).*

On saturating the alcoholic solution of the cyclopentenone (3 grams) and salicylaldehyde (3.2 grams) with hydrogen chloride at  $0^{\circ}$ , a dark red coloration develops; on keeping the mixture overnight, a yellow solid separates, which increases in quantity in the course of two days. The compound is almost insoluble in alcohol or glacial acetic acid, but dissolves sparingly in boiling nitrobenzene, from which it crystallises on cooling in yellow plates, which do not melt on heating to  $320^{\circ}$ ; it is insoluble in potassium hydroxide, even on boiling. The crystals have the remarkable property of fixing the solvent to such an extent that prolonged washing with boiling alcohol does not entirely remove the nitrobenzene. On account of this fact, the analytical results differed appreciably, especially in the values obtained for carbon, from the theoretical values, and it was not until the compound had been heated in a vacuum at  $160\text{--}170^{\circ}$  that the whole of the nitrobenzene was removed.

The substance is sparingly soluble in boiling chloroform; on cooling the concentrated solution it separates in yellow prisms. In this case also the solvent adheres to the solid; it can be removed, however, by heating in the steam-oven for several hours, or, more readily, by keeping for a short time in an air-bath at  $110\text{--}120^{\circ}$ :

0.2053 gave 0.6588  $\text{CO}_2$  and 0.0870  $\text{H}_2\text{O}$ .  $\text{C}=87.52$ ;  $\text{H}=4.70$ .

0.2044 „ 0.6558  $\text{CO}_2$  „ 0.0875  $\text{H}_2\text{O}$ .  $\text{C}=87.51$ ;  $\text{H}=4.76$ .

$\text{C}_{31}\text{H}_{23}\text{O}_2$  requires  $\text{C}=87.73$ ;  $\text{H}=4.72$  per cent.

The *spiropyran* compound dissolves readily in cold concentrated sulphuric acid, yielding a solution which appears deep red by transmitted light, and shows a very strong, deep green fluorescence.



*The Anhydride of 3:4-Diphenyl-2:5-di-β-hydroxy-α-naphthylidene-Δ<sup>3,4</sup>-cyclopentenone. (Diphenylacetylenedi-β-naphthaspiran) (IV).*

This substance is readily obtained by the method employed in the case of the above *spiro*-compound, namely, by the action of hydrogen chloride on the mixture of the *cyclopentenone* (2 grams), and *β*-naphthol-*α*-aldehyde (3 grams), dissolved in glacial acetic acid. The aldehyde was obtained for this purpose by means of the elegant method given by Gattermann for the preparation of aromatic aldehydes (Gattermann and von Horlacher, *Ber.*, 1899, **32**, 285).

The brown solid which is deposited when the mixture is allowed to remain for two days, dissolves fairly readily in boiling chloroform, but only sparingly in hot alcohol; it crystallises from the mixed solvents, on cooling, in brown prisms, which darken at 265° and are completely charred at 280°. The substance is quite insoluble in potassium hydroxide, even on boiling. For analysis, the compound was dried in an air-bath at 120°:

0.1993 gave 0.6510 CO<sub>2</sub> and 0.0795 H<sub>2</sub>O. C=89.13; H=4.43.

C<sub>30</sub>H<sub>24</sub>O<sub>2</sub> requires C=89.31; H=4.58 per cent.

Like the above, this *spiro*-compound dissolves in cold concentrated sulphuric acid to a deep red solution, which shows an intense green fluorescence.

*Action of p-Nitrosodiethylaniline on 3:4-Diphenylcyclopentenone.*

As already stated (p. 552), this reaction has been studied with the object of ascertaining whether 5-*p*-diethylaminoanilo-3:4-diphenyl-*Δ*<sup>3,4</sup>-cyclopentene-1:2-dione,  $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \cdot \text{C} \begin{smallmatrix} \diagup \text{CPh} \\ \diagdown \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{CPh} \\ \diagdown \text{CO} \end{smallmatrix}$ , behaves similarly to the corresponding compound, previously obtained (Ruhemann and Naunton, *T.*, 1912, **101**, 42) from nitroso-dimethylaniline, which in solution readily passes into the colloidal state.

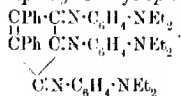
The *cyclopentenone* (5 grams) condenses with *p*-nitrosodiethylaniline (12 grams) when a little alcoholic potassium hydroxide is added to the mixture of the reagents dissolved in alcohol. On keeping for several days, a dark brown solid (6–7 grams) separates; this is sparingly soluble in cold, but fairly readily in boiling alcohol, forming a reddish-violet solution, which, on cooling, deposits violet-brown needles melting gradually at 170–171°:

0.2006 gave 0.5915 CO<sub>2</sub> and 0.1348 H<sub>2</sub>O. C=80.44; H=7.46.

0.1567 „ 16.8 c.c. N<sub>2</sub> at 20° and 751 mm. N=12.0.

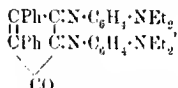
C<sub>17</sub>H<sub>20</sub>N<sub>2</sub> requires C=80.57; H=7.43; N=12.0 per cent.

The analytical results indicate that the compound is 1:2:3-tris-diethylaminoanilo-4:5-diphenyl- $\Delta^{3:5}$ -cyclopentene,



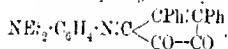
It corresponds, therefore, with the trisanilino-compound previously obtained by the action of nitrosodimethylaniline (*loc. cit.*), and its formation may be explained by the hypothesis already brought forward to account for the production of the latter compound.

It may be expected that, as in the case of the reaction between nitrosodimethylaniline and the cyclopentenone, a second condensation product,



formed by the interaction of the ketone and two molecules of nitrosodiethylaniline, is produced at the same time as the tris-diethylaminoanilo-compound; this substance may be contained in the mother liquor of the latter, which was not further examined.

5-p-Diethylaminoanilo-3:4-diphenyl- $\Delta^{2:4}$ -cyclopentene-1:2-dione,



The violet compound,  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_2$ , is easily decomposed by mineral acids (compare the behaviour of the analogous substance,  $\text{C}_{41}\text{H}_{40}\text{N}_6$ , *loc. cit.*), yielding a yellow solid, which, on warming with water, turns red. This substance is very soluble in chloroform, and moderately so in hot alcohol, from which it crystallises on cooling in red plates melting at  $217-218^\circ$ :

0.2062 gave 0.5980  $\text{CO}_2$  and 0.1125  $\text{H}_2\text{O}$ .  $\text{C} = 79.05$ ;  $\text{H} = 6.00$ .

0.2225 " 14.0 c.c.  $\text{N}_2$  at  $20^\circ$  and 747 mm.  $\text{N} = 7.06$ .

$\text{C}_{17}\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{C} = 79.41$ ;  $\text{H} = 5.88$ ;  $\text{N} = 6.86$  per cent.

The compound forms a hydrochloride, which dissolves readily in alcohol; on addition of platinic chloride to the solution, a platinic chloride is precipitated in yellow needles:

0.1461 gave 0.0233 Pt.  $\text{Pt} = 15.91$ .

$(\text{C}_{17}\text{H}_{12}\text{O}_2\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 15.86$  per cent.

The compound  $\text{C}_{17}\text{H}_{12}\text{O}_2\text{N}_2$  differs from the corresponding azomethine which is formed from nitrosodimethylaniline, in that its solutions in alcohol or chloroform do not yield gels.

*Action of isoAmyl Formate on  $\beta$ -Hydrindone.*

The  $\beta$ -hydrindone required for the following experiments was obtained, as in the recent research on triketohydrindene hydrate (T., 1911, **99**, 796), from 1-chloro-2-hydroxyhydrindene, according to the directions given by Heusler and Schiefer (*Ber.*, 1899, **32**, 28). On adding the solution of the ketone (5 grams) and isoamyl formate (8.8 grams) in absolute ether to sodium ethoxide (5.2 grams) suspended in ether, the whole being cooled to  $0^{\circ}$ , a blue coloration develops. After three days, the mixture is shaken with ice-water; a viscous product, insoluble in ether or water, separates out. The clear aqueous layer, on treatment with acetic acid, yields a red oil, from which no solid product could be extracted; nor could any crystalline substance be obtained from the original dark, ethereal extract. It follows, therefore, that no hydroxymethylene derivative of  $\beta$ -hydrindone is formed under these conditions, the ketone being completely decomposed.

*Formation of spiroPyran Compounds from  $\beta$ -Hydrindone.*

2-Hydrindone, like diphenylcyclopentenone, reacts both with salicylaldehyde and with 2-naphthol-1-aldehyde, yielding *spiro*-pyran compounds.

*The Anhydride of 1:3-Disalicylidene-2-hydrindone (Phenylene-dibenzospiropyran), (V).*

When the alcoholic solution of the hydrindone (2 grams) and salicylaldehyde (3.1 grams) is saturated with hydrogen chloride at  $0^{\circ}$ , the liquid sets after a short time to a red, semi-solid mass, which cannot be separated by filtration; it is therefore allowed to dry on a porous plate. The substance is sparingly soluble in hot alcohol, more readily in boiling chloroform; on cooling, it separates from the latter solvent in deep red prisms, which melt gradually at  $260-261^{\circ}$ .

For analysis the substance must be freed from traces of chloroform by heating in an air-bath to  $115-120^{\circ}$ ; the solvent adheres to the compound to such an extent that prolonged heating in the steam-oven is necessary to remove it:

0.1582 gave 0.4980  $\text{CO}_2$  and 0.0610  $\text{H}_2\text{O}$ . C = 85.85; H = 4.28.

$\text{C}_{23}\text{H}_{14}\text{O}_2$  requires C = 85.71; H = 4.35 per cent.

The solution of this substance in cold concentrated sulphuric acid appears brown by transmitted light; it shows a green fluorescence, which is not quite so strong as that observed with the corresponding compound obtained from diphenylcyclopentenone.

*The Anhydride of 1:3-Di-β-hydroxy-α-naphthylidene-2-hydrindone  
(Phenylenedi-β-naphthaspiropyran) (VI).*

This octacyclic *spiropyran* compound is prepared by the method employed in the case of the above substance. On treatment of the alcoholic solution of the ketone (2 grams) and 2-naphthol-1-aldehyde (5.8 grams) with hydrogen chloride at 0°, a deep blue coloration is developed, and a black solid is deposited. After two hours, this is collected and washed with alcohol, in which it is insoluble. It dissolves in boiling glacial acetic acid to a reddish-violet solution, from which it separates slowly on cooling in small, bluish-black prisms, which undergo no perceptible change on being heated to 320°. For analysis the substance was dried at 120°:

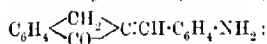
0.1978 gave 0.6395 CO<sub>2</sub> and 0.0745 H<sub>2</sub>O. C = 88.17; H = 4.18.

C<sub>31</sub>H<sub>18</sub>O<sub>2</sub> requires C = 88.15; H = 4.27 per cent.

The solution of this compound in cold concentrated sulphuric acid is deep red and only faintly fluorescent; on boiling, however, an intense fluorescence is developed.

*The Action of o-Aminobenzaldehyde on 1-Hydrindone.*

This reaction occurs on addition of a few drops of alcoholic potassium hydroxide to the mixture of the aldehyde (4.5 grams) and the hydrindone (5.1 grams), dissolved in alcohol. The solution becomes red, and after a few minutes a yellow solid separates. This is sparingly soluble in cold alcohol, moderately so in boiling, and crystallises on cooling in orange prisms melting at 202–205°. The compound is 2-*o*-aminobenzylidene-1-hydrindone,

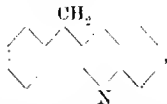


0.2087 gave 0.6240 CO<sub>2</sub> and 0.1080 H<sub>2</sub>O. C = 81.54; H = 5.75.

0.2265 „ 12.2 c.c. N<sub>2</sub> at 17° and 746 mm. N = 6.13.

C<sub>16</sub>H<sub>13</sub>ON requires C = 81.70; H = 5.53; N = 5.96 per cent.

In addition to 2-*o*-aminobenzylidene-1-hydrindone, indenoquinoline,



is formed in this reaction. This substance is obtained in the mother liquor after the separation of the above compound, and is precipitated as a white solid on the addition of water. It crystallises from dilute alcohol in colorless needles melting at 170–171°.

0.2080 gave 0.6745  $\text{CO}_2$  and 0.0940  $\text{H}_2\text{O}$ .  $\text{C}=88.44$ ;  $\text{H}=5.13$ .

0.2095 " 11.8 c.c.  $\text{N}_2$  at  $18^\circ$  and 761 mm.  $\text{N}=6.61$ .

$\text{C}_{16}\text{H}_{11}\text{N}$  requires  $\text{C}=88.48$ ;  $\text{H}=5.07$ ;  $\text{N}=6.45$  per cent.

The same compound is formed, also, if a little concentrated hydrochloric acid is added to 2-*o*-aminobenzylidene-1-hydrindone dissolved in alcohol, and the solution evaporated to small bulk on the water-bath. In the course of a few hours, colourless needles of the hydrochloride of the quinoline separate. This salt is unstable, and gradually dissociates, on boiling with water, into hydrochloric acid and the free base; but if platinum chloride is added to the alcoholic solution a light yellow platinumchloride is precipitated, which decomposes at about  $270^\circ$ :

0.2320 gave 0.0535 Pt.  $\text{Pt}=23.06$ .

$(\text{C}_{16}\text{H}_{11}\text{N}_2)_2\text{H}_2\text{PtCl}_6$  requires  $\text{Pt}=23.05$  per cent.

Indenoquinoline was obtained by Noelting and Blum (*Ber.*, 1901, **34**, 2471), who described it under the name quinolylenphenylene-methane. These authors prepared the compound by the distillation of the corresponding ketoindenoquinoline with a mixture of zinc and zinc oxide; they gave the melting point as  $166-167^\circ$ , and fixed the composition by a nitrogen determination only.

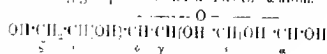
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## LXIV.—*Partially Methylated Glucoses. Part I.* *ξ-Monomethyl Glucose and γξ-Trimethyl Glucose.\**

By JAMES COLQUHOUN IRVINE and JAMES PATTERSON  
SCOTT, M.A., D.Sc. (Carnegie Fellow).

DERIVATIVES of sugars in which only some of the hydroxyl groups are substituted are, of course, well known, but in many cases it is probable that substances of this nature described in the literature

\* The method adopted in this and the succeeding paper to indicate the position of substituting groups in the sugar molecule differs from that hitherto in use, as the carbon atom of the reducing group is now indexed as the α-atom.



It will be seen that the oxygen ring-system invariably termed the "γ-oxidizing ring") now connects the α- and δ-atoms, and thus all references in previous papers to the position of substituting groups are rendered inaccurate (see T., 1913, **103**, 41, 243; 1912, **101**, 1128, 1146; *Ann. Reports*, 1912, **9**, 95).

The authors wish it to be understood that they are not responsible for this inconsistency (see T., 1913, **29**, 69).

are merely mixtures and not individual compounds; thus, complete series of acetylated and benzoylated glucoses have been at various times described, but, considering the methods of preparation and the nature of the products, it is difficult to imagine that definite compounds were isolated. In general, the action on a sugar of excess of a reagent, which attacks hydroxyl groups, is to give a fully substituted derivative, whilst with restricted proportions of the same reagent, complex mixtures are formed which, as a rule, cannot be completely separated. This has naturally imposed limitations on the study of the individual asymmetric systems of the sugar molecule.

The hydroxyl groups in glucose may be differentiated into three classes, namely, (1) the reducing group, (2) the three remaining secondary alcohol groups, and (3) the terminal primary alcohol group. The first-mentioned group takes part in glucoside formation, and its special reactivity is also shown in many other reactions. Until recently, there seemed little necessity to distinguish sharply between the classes (2) and (3) mentioned above, but the preparation by Fischer of derivatives of  $\zeta$ -aminoglucose (*Ber.*, 1912, **45**, 3763) involves a striking instance of the special reactivity of the primary alcohol group. It is possible that the study of the sugars may be profitably extended, and the significance of configuration may become more fully apparent by examination, as far as possible, of the characteristics of each individual hydroxyl group present in the molecule and of the asymmetric system to which it belongs. It is with this object in view that we have undertaken the examination of a series of partly methylated glucoses.

In compounds of the type of tetramethyl glucose, the reactivity of the molecule is practically confined to the reducing group. On the other hand, in a partly methylated glucose the characteristic properties of the parent sugar are more closely preserved, and a greater variety of reactions are available. Moreover, owing to the increase of stability and solubility due to methylation, the more obscure decompositions undergone by unsubstituted sugars are, to a large extent, precluded.

The general method devised by Purdie and Irvine for the alkylation of sugars does not admit of the isolation of incompletely substituted derivatives other than compounds of the nature of  $\beta$ , $\gamma$ , $\epsilon$ -trimethyl glucose. In the first paper of the series, however, (*T.*, 1903, **83**, 1021) it was pointed out that, in order to protect a sugar from oxidation during the silver oxide reaction, all that is necessary is to substitute the reducing group by a condensed residue capable of subsequent removal by hydrolysis. For obvious reasons, compounds of the nature of methylglucoside have been largely made use of

for this purpose, but other types of sugar derivatives may also be employed. Of these, the compounds produced by the condensation of sugars with ketones or aldehydes are best adapted for the purpose required; for example, a glucosidic monoacetone derivative of a hexose must, irrespective of the linking of the acetone residue, contain three hydroxyl groups capable of methylation, so that hydrolysis of the alkylated product should give a trimethyl hexose; similar treatment of a diacetone derivative should result in a mono-methylated aldose or ketose. The remaining type of a partly methylated hexose would be represented by a dimethyl glucose, and this has now been prepared, as described in the succeeding paper, by alkylation of benzylidene methylglucoside, and removal of benzaldehyde and methyl alcohol by hydrolysis.

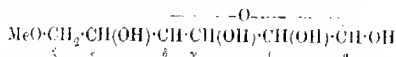
The principles outlined above have already been applied to the preparation of dimethyl rhamnose and monomethyl fructose (T., 1906, **89**, 1194; 1909, **95**, 1220), and are of wide application. It is thus possible, by the introduction of hydrolysable residues into the sugar molecule, to protect selected hydroxyl groups from alkylation. The process is also applicable to the preparation of similar derivatives from polyhydric alcohols.

The following table summarises the methods adopted in the preparation of the different types of methylated glucoses now known:

Condensed glucose derivative.	Number of methoxyl groups added.	Groups removed by hydrolysis.	Methylated glucose formed.
Glucosediacetone .....	1	Two mols. acetone	Monomethyl glucose
Benzylidene $\alpha$ -methylglucoside .....	2	Methyl alcohol and benzaldehyde	Dimethyl glucose
Glucosemonoacetone .....	3	One mol. acetone	Trimethyl glucose
Methylglucoside .....	4	Methyl alcohol	Tetramethyl glucose

### $\zeta$ -Monomethyl Glucose.

The constitution assigned to this compound will be discussed later, and it will be shown that the methoxyl group is most probably attached to the terminal carbon atom in the sugar chain, that is, in the position marked  $\zeta$  in the following formula:



The compound may therefore be termed  $\zeta$ -monomethyl glucose. The method of preparation was to methylate glucosediacetone by means of the silver oxide reaction, with the precautions found advisable in the case of the corresponding fructose derivative. The product consisted of monomethyl glucosediacetone, which was

purified by fractional distillation (b. p. 139–140°/12 mm.). The properties and solubilities of this compound resembled those of other methylated sugar derivatives of a glucosidic nature, but the fact that it is laevorotatory ( $[\alpha]_D^{20}$  –32.2° in alcohol) is worthy of note.

The removal of the acetone residues by hydrolysis took place with extreme ease. The course of the reaction was followed polarimetrically, and the results showed that both acetone groups were removed simultaneously and at apparently the same rate. The product of this reaction was monomethyl glucose, which showed all the characteristic properties of a reducing sugar. When crystallised from a mixture of methyl alcohol and acetone, the compound showed downward mutarotation, and this form is accordingly regarded as the  $\alpha$ -isomeride. The  $\beta$ -form of the sugar, showing upward mutarotation, was isolated by the method described in the experimental part. The mutarotatory changes shown by both forms in methyl alcoholic solution were:

Initial $[\alpha]_D^{20}$ of $\alpha$ -form.		Permanent $[\alpha]_D^{20}$ .		Initial $[\alpha]_D^{20}$ of $\beta$ -form.
+38.6	→	–68.6	←	+29.6

The nature of the solvent had very little effect on the magnitude of the initial rotations, and as the sugar showed suspended mutarotation in methyl alcohol it was possible to obtain accurate values for the initial readings. The above data, calculated in the form of molecular rotations, may thus be applied to test the generalisations established by C. S. Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 66) regarding rotatory power in the sugar group. If A and B represent the proportion of the molecular rotation due respectively to the reducing group and the remainder of the molecule, we have:

Monomethyl $\alpha$ -glucose.....	$[\alpha]_D = 19128 = A + B$
Monomethyl $\beta$ -glucose.....	$[\alpha]_D = 5752 = A + B.$

In this particular case, the sum (2B) should be different from the similar value obtained for glucose as the non-reducing part of the molecule is different. On the other hand, the difference (2A) should be identical. The figures are compared below:

	Sum (2B).	Difference (2A).
Glucose.....	23370	1626
Monomethyl glucose.....	21859	1776

The agreement with the calculated values is thus only approximate; in fact, the differences are proportionally more divergent than the sums. Possibly a closer agreement is not to be expected, as Hudson's rule is based on the assumption that the principle of optical superposition holds exactly. At the same time, it will be



shown in the succeeding paper that the optical values for dimethyl glucose show a much closer agreement with the figures calculated by Hudson's method. It would thus appear that his generalisation applies, approximately at least, to sugars in which the hydroxyl positions are methylated. Doubtless the values we ascribe to the initial rotations of monomethyl  $\beta$  glucose are not strictly accurate. The  $\alpha$  form was certainly obtained in the pure state, but this cannot be claimed for the  $\beta$ -isomeride, which was only isolated in small amount. Accordingly, if the difference (2A) be adjusted to the calculated value (16,200), the theoretical initial specific rotation for the  $\beta$ -form becomes  $+15.1^\circ$ , in place of the recorded value  $\pm 29.6^\circ$ .

Extending these considerations to other methylated glucoses we find, as stated, that Hudson's rule applies to dimethyl glucose. Unfortunately, trimethyl glucose has only, so far, been obtained as a syrup, and all our attempts to isolate the pure  $\beta$ -form of tetramethyl glucose failed. If, however, the validity of Hudson's method be accepted, the initial specific rotation of  $\beta$ -tetramethyl  $\beta$ -glucose becomes  $+32.16^\circ$ . The adoption of this value can be justified on other grounds, as the specific rotations of the  $\alpha$  and  $\beta$  tetramethyl methylglucosides are known. Now, in comparing a sugar with its glucosides, the sum (2B) should be constant, whilst the difference (2A) should vary. The value for 2B should thus be identical for the fully alkylated glucosides and tetramethyl glucose. This is shown below to be essentially the case.

*Sum of Molecular Rotations.*

Tetramethyl methylglucosides	32515 (found)
Tetramethyl glucoses	31380 (value for the $\beta$ -form calculated).

The discrepancy is thus slightly over 3 per cent., which is well within the limits of the experimental error. The following table gives the corrections of some of our experimental results indicated by applying Hudson's method:

	Found.	Calculated.
$\zeta$ Monomethyl $\beta$ -glucose	$[\alpha]_D^{20} + 29.6$	$-15.1$
$\beta$ - $\zeta$ Tetramethyl $\beta$ -glucose	not isolated	$+32.16$
$\beta$ -Dimethyl $\alpha$ -glucose	$-81.44$	$+83.80$

*Constitution of Monomethyl Glucose.*

The sugar resembled monomethyl fructose in general properties, and was converted into the same monomethylglucosazone. This at once indicates that the methyl group is attached to the terminal carbon atom. It should be stated, however, that the constitution of monomethyl fructose is not rigidly established, as the evidence

afforded by oxidation is capable of a double interpretation. The methyl group may, in fact, be situated either in the  $\gamma$  or  $\zeta$  positions. The former alternative is, however, completely at variance with the results obtained in the study of the isomeric fructose monoacetones (T., 1910, 97, 1277), and is in the meantime unsupported by any positive evidence.

*$\gamma\epsilon\zeta$ -Trimethyl Glucose.*

One form of a trimethyl glucose (*loc. cit.*, and T., 1903, 83, 1037), in which the methyl groups are present in positions  $\beta\gamma\epsilon$ , has already been described. In the course of the present research, the isomeric  $\gamma\epsilon\zeta$ -trimethyl glucose was also prepared.

Glucosemonoacetone, on complete methylation, was converted into trimethyl glucosemonoacetone (b. p. 138–139°/12 mm.). The isolation of the liquid product was accompanied by slight hydrolysis of the acetone residue, so that the optical values have little significance, but the fact that the compound is levorotatory is nevertheless remarkable. The hydrolysis was carried out in the usual manner, but as the sugar could not be obtained crystalline the syrup examined consisted of a mixture of  $\alpha$ - and  $\beta$ -forms in equilibrium. The proportion of the  $\beta$  form was, however, increased by heating the compound at 70°, after which, on solution in alcohol, the following optical change was shown:

Initial specific rotation.	—————>—————	Permanent specific rotation.
-6.2°		-8.3.

The rotatory power of this sugar is in every respect abnormal. Whereas both the  $\alpha$ - and  $\beta$ -forms of glucose, and also of all other known methylated glucoses, are dextrorotatory, the equilibrium value for  $\gamma\epsilon\zeta$ -trimethyl glucose is levorotatory. Not only so, but the mutarotation recorded above indicates that the  $\alpha$ -form is also levorotatory, as the change  $\beta \rightarrow \alpha$  results in an increase of rotation in the *levo*-sense. This is at variance with all other optical values obtained for the glucoses, and admits of no simple explanation. The preparation of the sugar has been repeated on two occasions by independent workers, who have verified our results, and the possibility that methylation in the  $\gamma$ -position of the glucose molecule is attended with great alterations in rotatory power is being further investigated by one of us (Dr. Scott).

### EXPERIMENTAL.

*Preparation of Glucosediacetone and Glucosemonoacetone.*

Considerable difficulty was experienced in preparing a sufficient quantity of glucosediacetone, and accordingly the directions given

by Fischer (*Ber.*, 1895, **28**, 1145, 2496) were modified. All the operations involved in converting the sugar into the corresponding dimethylacetal were conducted in Winchester bottles, so that the syrupy product could afterwards be thoroughly incorporated with the acetone used in the subsequent condensation. In each experiment, 30 grams of glucose were used, and the crude dimethylacetal was obtained in the form of a syrup adhering to the sides of the bottle. Fragments of porous tile were added, and the mixture was vigorously shaken for six hours with a large excess of acetone containing 0.25 per cent. of hydrogen chloride. The solution was thereafter preserved for thirty-six hours in an incubator at 33°, with occasional periods of shaking. The free acid was then removed by means of silver carbonate, the solution shaken with charcoal, and the solvent removed in a vacuum.

In our experience, the syrup thus obtained consisted of a mixture of the di- and mono-acetone derivatives, the former being in excess, and crystallised completely on cooling. The solid mass was finely powdered and extracted repeatedly with a large excess of petroleum of low boiling point until all the glucosediacetone had been removed, after which the insoluble residue, consisting essentially of the mono-acetone compound, was recrystallised from dry ethyl acetate. The two products were thus obtained in one operation, and, as the combined yield amounted to 30 per cent. of the glucose used, the efficiency of the process was practically doubled.

#### *Methylation of Glucosediacetone.*

Owing to the ease with which the acetone residues are removed from glucosediacetone, several precautions were necessary in carrying out the methylation. The method actually adopted was essentially the same as that already described (*loc. cit.*) for the methylation of fructosediacetone by the silver oxide process, and the proportions of the reacting materials employed were identical. In isolating the methylated product it was found to be of the utmost importance to use ether free from traces of acid, and to avoid prolonged boiling with the solvent.

After drying the ethereal extract by means of sodium sulphate and removal of the solvent, the theoretical amount of a neutral oil remained, which was fractionated in a vacuum. After two distillations the main fraction boiled at 139–140°, 12 mm., and consisted of pure monomethyl glucosediacetone.

\*Found: C 56.54; H 7.99; OMe 11.60.

$C_{12}H_{20}O_5(OMe)$  requires C 56.93; H 8.03; OMe 11.31 per cent.

The following observations were made on the optical activity of the substance:

Solvent.	$c$ .	$l$ .	$\alpha_{20}$	$[\alpha]_D^{20}$
Ethyl alcohol.....	5.65	2	3.25	-32.17
Acetone .....	5.92	2	3.19	-31.78

*Monomethyl glucosediacetone* is a colourless, mobile, highly refractive liquid, which has no action on Fehling's solution until after hydrolysis. The compound is readily soluble in the ordinary organic solvents, but only sparingly so in water. On heating a solution of the compound in 50 per cent. alcohol, containing 0.1 per cent. of hydrogen chloride at 80°, the acetone groups were completely removed in twelve hours. During this time the rotation altered regularly from *levo* to *dextro*, and, as the curve representing the change showed no break, it may be concluded that both ketonic residues are removed simultaneously and at the same rate.

#### *Monomethyl Glucose.*

A 5 per cent. solution of monomethyl glucosediacetone in a large excess of 50 per cent. aqueous alcohol containing 0.4 per cent. of hydrogen chloride was heated in boiling water for one hundred and five minutes. The acid was removed with silver carbonate, after which the solution was shaken with charcoal, filtered, and evaporated to a syrup at 35°/15 mm. The residue was then dissolved in methyl alcohol, and the solution allowed to evaporate spontaneously in a vacuum desiccator. After twelve hours, monomethyl glucose commenced to separate in the form of a crystalline crust and the bulk of the product was isolated by the addition of acetone to the solution, a procedure which promoted the separation of the  $\alpha$ -form in excess. The yield of crystalline product was 50 per cent. of the monomethyl glucosediacetone used in the hydrolysis.

Found: C=43.24; H=7.13; OMe=15.74.

$C_6H_{12}O_5(OMe)$  requires C=43.30; H=7.22; OMe=15.98 per cent.

*Monomethyl glucose* is readily soluble in water, less so in methyl alcohol, and very sparingly soluble in other organic solvents. It reduces Fehling's solution readily on warming.

#### *Isolation of $\alpha$ - and $\beta$ -Forms of Monomethyl Glucose.*

When the sugar was crystallised from methyl alcoholic solution only the  $\alpha$ -form separated. The product thus obtained crystallised in short, rectangular plates, which melted sharply at 157–158°, and showed extensive mutarotation in aqueous solution. The same form of the sugar was precipitated in the crystalline state by the

cautious addition of acetone to a methyl-alcoholic solution, but, as afterwards explained, successive crops are liable to contain increasing amounts of the  $\beta$ -form.

*Mutarotation of  $\zeta$ -Monomethyl  $\alpha$ -Glucose.*

Solvent.	c.	Mutarotation.
Water.....	2.424	96.7° $\rightarrow$ +55.5°
Methyl alcohol.....	1.684	98.6° $\rightarrow$ 68.0

Equilibrium was established very rapidly in aqueous solution, and the permanent rotation was recorded eleven minutes after the first reading.\* On the other hand, the compound exhibited suspended mutarotation in methyl alcohol, and the change was only apparent on the addition of a trace of alkali.

*$\zeta$ -Monomethyl  $\beta$ -Glucose.*—A 30 per cent. solution of the  $\alpha$ -form of the sugar in methyl alcohol was boiled under a condenser until the equilibrium  $\alpha \rightleftharpoons \beta$  had been established. The bulk of the solvent was then removed at the ordinary pressure until a mobile syrup remained. On adding small quantities of acetone, the sugar in solution was precipitated in two fractions, the first of which consisted entirely of the  $\alpha$ -form. The more soluble crop was a mixture of both isomerides, whilst the mother liquor deposited crystalline nuclei of the  $\beta$ -form.

The process described above was therefore repeated, and the bulk of the  $\alpha$ -sugar precipitated as usual. After filtration, nuclei of the  $\beta$ -form were added to the filtrate, and a small, apparently homogeneous crop of the  $\beta$ -isomeride separated.

*Monomethyl  $\beta$ -glucose* crystallises in delicate, prismatic needles, which are extremely soft and friable, and melt at 130°–132°. The mutatory changes observed are given below:

Solvent.	c.	Initial $[\alpha]_D^{20}$ .	Final $[\alpha]_D^{20}$ .
Water.....	1.689	31.9° $\rightarrow$	+55.1°
Methyl alcohol.....	1.680	28.0° $\rightarrow$	68.9

The end-points are thus in satisfactory agreement with those recorded for the  $\alpha$ -form.

*$\zeta$ -Monomethyl Methylglucoside.*

This compound was prepared by Fischer's process, a 5 per cent. solution of monomethyl glucose in methyl alcohol containing 0.25 per cent. of hydrogen chloride, being heated for sixty hours at 100°. The product was worked up in the usual manner, and was isolated as a viscous syrup, for which no crystallising medium could be found. The compound was ultimately analysed without

\* The speed of this change suggests that a catalyst was accidentally present.

further purification. During the dehydration of the analysis sample constant weighings were only obtained after heating for five hours in a vacuum at 100°. This treatment apparently effected some decomposition, as the analytical figures obtained were only approximate.

Found: C=46.70; H=7.79; OMe=27.0.

$C_6H_{10}O_4(OMe)_2$  requires C=46.15; H=7.69; OMe=29.8 per cent.

*Monomethyl methylglucoside* is extremely soluble in water, and the usual organic solvents with the exception of hydrocarbons. It behaves as a glucoside towards Fehling's solution, and shows, for  $c=1.973$ ,  $[\alpha]_D +99.3^\circ$  in ethyl alcohol. This value has little significance, as it is determined on the equilibrium mixture of the  $\alpha$  and  $\beta$ -forms.

#### 5. *Monomethylglucosazone.*

The methylated sugar was dissolved in the minimum amount of 50 per cent. acetic acid, and mixed with a slight excess of phenylhydrazine acetate similarly dissolved. On heating the solution to 100° for three or four minutes and cooling, an abundant crop of yellow needles separated. After crystallisation from aqueous alcohol the compound melted at 161–165°, and analysis showed it to be monomethylglucosazone.

Found: C=61.05; H=6.72; OMe=7.0.

$C_{11}H_{21}O_5N_4(OMe)$  requires C=61.21; H=6.45; OMe=8.3 per cent.

The similarity of the osazone with that previously isolated from monomethyl fructose (*loc. cit.*) was so great as to suggest the identity of the two compounds, although the melting point now found was considerably higher. The value quoted in our previous paper was 142–144°, but this seems due to a clerical error. Fortunately, some of the original osazone was available for comparison. Both preparations, when examined under parallel conditions, melted at the same temperature (164°), and a mixture of the two gave the same melting point. As the specific rotation in ethyl alcohol ( $[\alpha]_D -86.7^\circ$  for  $c=0.5$ ) was also the same for each compound, there is no doubt that the two preparations are identical.

#### 6. *Trimethyl Glucose.*

*Methylation of Glucosemonoacetone.*—Before methylation, the glucosemonoacetone was twice recrystallised from neutralised ethyl acetate. It then melted at 154–155°, and showed  $[\alpha]_D -9.6^\circ$  in aqueous solution, values which differ slightly from those quoted by Fischer. The same precautions were adopted during the methylation as were employed in the case of glucosediacetone.

A 6 per cent. solution of the monoacetone compound (1 mol.) in dry acetone was mixed with methyl iodide (6 mols.), and silver oxide (3 mols.) gradually added. The reaction, which was at first vigorous, was continued by boiling gently on a water-bath for five hours. After extraction of the product with ether and removal of the solvent in a vacuum, a colourless syrup remained, which was freely soluble in methyl iodide. No extraneous solvent was thus required in the second methylation, in which the proportion of alkylating mixture was doubled. The product, isolated in the usual manner, was distilled under diminished pressure, and subjected to a third methylation, after which the main fraction boiled at 138–139°/12 mm. Contrary to expectation, the yield of volatile material was small, and a considerable residue remained behind in the flask. Moreover, the distilled liquid had acquired a perceptible action on Fehling's solution. It was thus evident that hydrolysis had taken place to some extent during the distillation, and this view was confirmed by analysis.

Found: C=53.52; H=8.17; OMe=37.98.

$C_9H_{18}O_8(OMe)_3$  requires C=54.96; H=8.17; OMe=35.50 per cent.

The results are thus intermediate between those calculated for trimethyl glucosemonoacetone and its hydrolysis product.

Solvent: methyl alcohol.  $c=3.77$ ,  $[\alpha]_D -27.2^\circ$ .

*Hydrolysis of Trimethyl Glucosemonoacetone.*—On heating a dilute solution of the above compound in aqueous alcohol containing 0.5 per cent. of hydrogen chloride for seventy-five minutes at 100°, the lavo-rotation diminished to a constant value. The further treatment was as usual, and the resulting colourless syrup, which could not be rendered crystalline, was analysed after drying at 70°/15 mm. until constant in weight.

Found: C=49.12; H=8.11; OMe=42.0.

$C_6H_{12}O_6(OMe)_3$  requires C=48.75; H=8.11; OMe=41.9 per cent.

The sugar, which is very soluble in water and in organic solvents, reduces Fehling's solution actively. The following observations on the optical activity of the substance were made on a specimen which had been heated for forty-five minutes at 70°:

Solvent.	$c$ .	$l$ .	Initial $[\alpha]_D^{20}$ .	Final $[\alpha]_D^{20}$ .
Water	4.39	2	7.52	8.32
Ethyl alcohol.	4.67	2	6.20	8.34

No crystalline derivative of the compound could be isolated. The sugar was resimified by phenylhydrazine and even condensation with aniline, which usually proceeds smoothly with methylated





The methylation of  $\epsilon$ -*D*-benzylidene  $\alpha$ -methylglucoside was carried out by the silver oxide reaction. No other process is, in fact, available, as the compound is exceedingly easily hydrolysed by acids, and also to some extent by alkalis. The alkylation proceeded with unusual smoothness. The product, which was readily obtained in the crystalline state, melted at 122--123°, and showed  $[\alpha]_D +97.03^\circ$  in acetone solution.

It was possible, by carefully regulated hydrolysis, to remove the aromatic residue without affecting the glucosidic group, the product of this reaction being  $\beta$ -*D*-dimethyl  $\alpha$ -methylglucoside, which was isolated in the usual manner. The alkylated glucoside melted at 80--82°, and showed practically the same specific rotation (142.6°) in aqueous and in acetone solution. When boiled with dilute hydrochloric acid, the glucosidic group was removed with the formation of dimethyl glucose, which was isolated in the form of a crystalline solid. After crystallisation from ethyl acetate, the sugar separated in well-developed prisms, which gave satisfactory analytical figures, but which melted very indefinitely. This behaviour was shown to be due to the presence of the stereoisomeric  $\alpha$ - and  $\beta$ -forms, both of which were ultimately isolated.

When the crystallisation from ethyl acetate was carried out from solutions containing not more than 5 per cent. of the solute, the sugar separated in clusters of delicate, pointed prisms. This proved to be the pure  $\beta$ -form (m. p. 108--110°), and thus showed upward mutarotation when dissolved in water, alcohol, or acetone. The details of these optical changes are given in the experimental part. The sugar exhibited suspended mutarotation in acetone solution, and it was therefore possible to obtain an exact record of the whole range of the change in this solvent.

The  $\alpha$  form of the sugar crystallised, along with the  $\beta$ -isomeride, from solutions in ethyl acetate containing from 7 to 10 per cent. of the solute. Separation of the two varieties was, however, best effected by cautious precipitation, from the equilibrium solution in alcohol, by the gradual addition of ether. The first crops to separate consisted, as before, of the  $\beta$  form, but, from the mother liquors, the  $\alpha$ -isomeride (m. p. 85--87°) was deposited in warty aggregates of microscopic prisms. This form showed extensive downward mutarotation in acetone solution.

Dimethyl glucose is thus well adapted for the study of mutarotation, as both stereoisomeric forms are available, and the ready solubility of the sugar, in solvents in which the change is slow, permits of the initial values being determined with much greater accuracy than in the case of an unsubstituted sugar.

*Discussion of Optical Results.*

The specific rotations of dimethyl glucose and its derivatives are only very slightly affected by the nature of the solvent employed. This is seen from the examples quoted below:

Solvent.	$\beta$ -Dimethyl $\beta$ -Glucose.	$\beta$ -Dimethyl $\alpha$ -Methylglucoside.
Water.....	+5.7°	+142.64°
Alcohol .....	5.7	143.63
Acetone .....	5.9	143.49

In this respect the compound resembles tetramethyl glucose, but the uniformity of the rotations in the different solvents is here even more marked. The nature of the solvent has, however, in the case of dimethyl glucose, a pronounced effect in altering the proportions of the mutarotatory  $\alpha$ - and  $\beta$ -forms which exist in equilibrium in solution. Thus, the equilibrium mixture in aqueous solution contains 77 per cent. of the  $\alpha$ -form and 23 per cent. of the  $\beta$ -isomeride. In acetone solution, on the other hand, the proportions are altered to 59 and 41 per cent. respectively.

Owing to the facility with which the true initial specific rotations of the  $\alpha$ - and  $\beta$ -forms of dimethyl glucose may be determined in acetone solution, the compound is a convenient one for testing the application of Hudson's rule (see preceding paper). The choice of acetone as a solvent for this purpose was determined by the facts, mentioned above, that the specific rotation of the sugar is practically unaffected by the nature of the solvent, and that the compound shows suspended mutarotation in this solvent. With regard to the accuracy of the optical values which we ascribe to the  $\alpha$ - and  $\beta$ -forms, there is little doubt that the latter isomeride was obtained in a pure condition, unmixed with the  $\alpha$ -form. On the other hand, the experimental difficulties encountered in isolating the  $\alpha$ -form were very great, and there is thus a possibility that the recorded specific rotation is lower than the true maximum. The discrepancy is, however, probably small.

Applying Hudson's principle, that the proportion of the molecular rotation of a sugar contributed respectively by the reducing group and the remainder of the molecule may be represented by  $A$  and  $B$ , the following equations are derived:

$$\begin{array}{llll} \beta\text{-Dimethyl } \alpha\text{-glucose} & \dots & [M] & 17.41 & A + B \\ \beta\text{-Dimethyl } \beta\text{-glucose} & \dots & [M] & 12.7 & A - B \end{array}$$

The sum of the molecular rotations ( $2B$ ) thus equals 18.268, and the difference ( $2A$ ) equals 15.814. The particular case now under consideration resembles that of monomethyl glucose, in that the value of  $2B$  should differ from that determined for glucose, whilst,

if Hudson's rule applies to substituted sugars, 2.4 should be a constant irrespective of the methylation of the non-reducing hydroxyl groups. These values are compared below:

	Sum of Molecular Rotations (2 <i>B</i> ).	Difference of Molecular Rotations (2 <i>A</i> ).
Glucose.....	23040	16200
Dimethyl glucose..	18268	15314

It will thus be seen that the value actually found for 2.4 differs only by slightly over 2 per cent. from that calculated according to Hudson's method. Taking into consideration the fact that extreme accuracy cannot be claimed for the specific rotation of the  $\alpha$ -form, the conclusion may reasonably be drawn that the generalisation is supported by this result. An alteration of the initial rotation of  $\alpha$ -dimethyl glucose from  $[\alpha]_D + 81.93^\circ$  to  $83.80^\circ$  would, in fact, give the calculated value (16200) for 2.4.

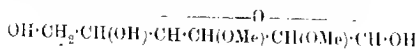
It may be mentioned that Hudson's method of calculation does not seem applicable to the case of the  $\alpha$ - and  $\beta$ -forms of benzylidene methylglucoside, where the difference (2.4) should equal that calculated from the activities of the methylglucosides. The values actually found are, however, far apart.

	Sum (2 <i>B</i> ).	Difference (2.4).
Methylglucosides .....	24571	36729
Benzylidene methylglucosides	2820	45129

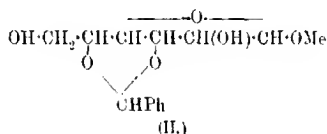
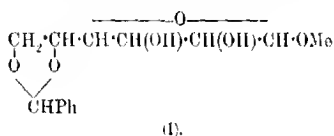
The introduction of the new asymmetric ring system into the molecule seems to exclude the application of Hudson's rule, but a definite decision on this point must be withheld until both stereoisomeric forms of benzylidene  $\beta$ -methylglucoside have been isolated. From the comparatively small difference in rotation shown by *d*- and *l*-benzylidene  $\alpha$ -methylglucoside, it is, however, most unlikely that any agreement will be found.

#### *Constitution of Dimethyl Glucose.*

Considerable difficulty was experienced in determining the constitution of the sugar, as there are six possible isomeric dimethyl glucoses possessing reducing properties, and each should exist in two stereoisomeric modifications. Experimental methods for determining the position of substituting groups in the sugar molecule are far from satisfactory, but the bulk of the evidence points to the following structure as the most probable:

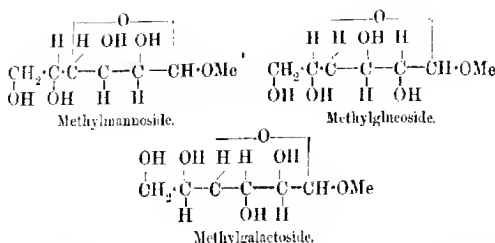


As the compound is a reducing sugar and shows mutarotation, no methyl groups can be attached to the carbon atoms indexed  $\alpha$  and  $\delta$ . The sugar, moreover, formed no osazone, but a dimethyl glucosphenylhydrazone was produced under conditions favourable to osazone formation. One methyl group must therefore be attached in position  $\beta$ . The allocation of the remaining methyl group can only be arrived at indirectly by consideration of the possible structures for benzylidene methylglucoside. From the evidence quoted above, the possible formulae for this substance are limited to three, of which the two most probable are the following:



The remaining possibility, in which the benzylidene residue couples the carbon atoms  $\gamma$  and  $\zeta$ , may be reasonably left out of consideration, as it includes a seven-membered ring. Comparing the two structures shown above, it will be seen that the formation of a substance possessing formula II would not only involve the production of a six-membered ring, but the condensation of the benzaldehyde would in such case take place with hydroxyl groups situated in the *trans*-position with reference to the plane of the  $\gamma$ -oxidic ring.\* Arguments have already been given (T., 1910, **97**, 1277) to show that this stereochemical arrangement results in considerable molecular strain, and is unlikely to occur when more stable positions are available for condensation. On the other hand, the hydroxyl groups attached to the carbon atoms  $\epsilon$  and  $\zeta$  are in the most favourable position for ring formation, and consequently we have selected formula I as the most suitable. This conclusion receives strong support from the following considerations. In methylglucoside, methylmannoside, and methylgalactoside, the same number of hydroxyl groups are in each case available for condensation with benzaldehyde, but their stereochemical arrangement is different:

\* See footnote to title of preceding paper, p. 564.



In methylmannoside, the pairs of hydroxyl groups attached to the carbon atoms  $\beta$ ,  $\gamma$ , and  $\epsilon$ ,  $\zeta$ , are in the most suitable position for ring formation admitted by the configuration. In methylglucoside and methylgalactoside, this is only true of the pair  $\epsilon$ ,  $\zeta$ . It can scarcely be a mere coincidence that methylmannoside readily forms both a mono- and a di-benzylidene compound, whilst methylglucoside and methylgalactoside, irrespective of the conditions of the reaction, give only monobenzylidene derivatives.

We thus conclude that in benzylidene methylglucoside, positions  $\epsilon$  and  $\zeta$  are protected from methylation, and that the methyl groups in dimethyl glucose occupy positions  $\beta$  and  $\gamma$ . This structure is in strict agreement with all the properties of the sugar, including its behaviour towards phenylhydrazine. The above considerations, which indicate that the condensation reactions of all the hydroxyl groups in sugars and glucosides are controlled by stereochemical arrangement, are capable of considerable application, and work in this direction is being continued.

#### EXPERIMENTAL.

##### *Preparation of $\epsilon$ -Benzylidene $\alpha$ -Methylglucoside.*

Methylglucoside was condensed with benzaldehyde by the process described by Alberola van Ekenstein (*loc. cit.*). It is, however, quite unnecessary to use sodium sulphate in the reaction, or to take any other precaution to remove the water formed in the condensation; the benzaldehyde used should be very carefully fractionated. The best yields were obtained when the glucoside (50 grams) was finely powdered and sifted through muslin, mixed with a large excess of the aldehyde (300 c.c.), and heated for three hours at 115°. Thereafter, the temperature was maintained at 160° for nine hours. The product was precipitated by the addition of light petroleum, and crystallised from hot water. Yield, 25 per cent. of the glucoside used.

*Isolation of  $\epsilon$ -D-Benzylidene  $\alpha$ -Methylglucoside.*

In the course of several consecutive preparations of benzylidene methylglucoside, the crude product was precipitated as usual by the addition of light petroleum to the solution in benzaldehyde. The united mother liquors were put aside for several hours, when a small second crop of crystals was gradually deposited. On recrystallising this product from hot water, it was at once seen that the material did not consist of Alberda van Ekenstein's compound, as the latter separates in long, flexible needles, which form on the surface of the solution. In this case, the product crystallised on the bottom of the basin in small, warty aggregates of stout prisms, which were analysed after a second crystallisation:

Found, C = 59.35; H = 6.51; OMe = 11.6.

$C_{13}H_{15}O_6(OMe)$  requires C = 59.55; H = 6.38; OMe = 11.0 per cent.

The constants of the two isomerides are compared below:

Alberda van Ekenstein's Compound.	New Isomeride.
<i>l</i> -Benzylidene $\alpha$ -Methyl- <i>d</i> -glucoside.	<i>d</i> -Benzylidene $\alpha$ -Methyl- <i>d</i> -glucoside.
M. p. 161–162°	145–149°
$[\alpha]_D^{20} + 85.0^\circ$	– 96.01°
Crystalline form: needles.	prisms.
Less soluble form.	More soluble form.

*Methylation of *l*-Benzylidene  $\alpha$ -Methylglucoside.*

The material used in the alkylation was the isomeride melting at 161–162°. A solution of 30 grams of the benzylidene compound (1 mol.), in 80 c.c. of acetone, was mixed with 150 grams of methyl iodide (10 mols.), and 123 grams of silver oxide (5 mols.) were gradually added. The reaction was completed by heating on a water-bath for six hours. Next morning, large crystals of the product, measuring several centimetres, were found imbedded in the silver iodide. These were readily soluble in boiling acetone, and crystallised from the solution on concentration and cooling. After recrystallisation from light petroleum, the pure compound weighed 32.5 grams, so that the yield was practically quantitative:

Found, C = 61.93; H = 7.21; OMe = 28.2.

$C_{13}H_{15}O_6(OMe)_3$  requires C = 61.93; H = 7.10; OMe = 30.0 per cent

$\epsilon$ -Benzylidene  $\beta$ -dimethyl  $\alpha$ -methylglucoside crystallises in prisms, melting at 122–123°. It is very sparingly soluble in water, but is readily dissolved by organic solvents.

Solvent: acetone;  $c = 1.640$ ;  $[\alpha]_D^{20} = 97.05$ .

*Partial Hydrolysis of Benzylidene Dimethyl Methylglucoside.*

A 10 per cent. solution of the above compound in 1 per cent. aqueous hydrochloric acid was heated, with frequent shaking, at 95° for one hour. The reaction was conducted under a condenser, through which a current of carbon dioxide was passed. The benzaldehyde formed was removed by extraction with ether, the aqueous liquor neutralised with barium carbonate, and the filtrate evaporated to dryness at 45°/15 mm. The residue was then extracted with acetone, and the filtrate concentrated to a syrup, which solidified on cooling. Purification of the crude product was effected by several recrystallisations from benzene, a large excess of the solvent being employed. During the purification, an oil separated in the first instance from the dilute benzene solution; this was allowed to settle, after which the decanted solution was concentrated to the crystallising point. Throughout these operations moisture must be rigidly excluded until all hygroscopic by-products have been eliminated. Thirteen grams of pure dimethyl methylglucoside, melting at 80–82°, were thus obtained from 20 grams of benzylidene dimethyl methylglucoside:

Found: C=48.46; H=8.26; OMe=39.8.

$C_6H_2O_5(OMe)_3$  requires C=48.65; H=8.11; OMe=41.9 per cent.

$\beta$ -Dimethyl  $\alpha$ -methylglucoside is readily soluble in water and organic solvents generally, sparingly so in ether or benzene, insoluble in hydrocarbon solvents. The compound reduced Fehling's solution only after hydrolysis, and displayed no mutarotation in solution:

Solvent.	c.	l.	$\alpha_D^{20}$ .	$[\alpha]_D^{20}$ .
Water.....	5.08	1	+7.25	+142.64
Ethyl alcohol..	5.07	1	7.26	143.08
Acetone.....	4.25	2	12.21	143.49

*Hydrolysis of  $\beta$ -Dimethyl  $\alpha$ -Methylglucoside.*

The conversion into dimethyl glucose was carried out by boiling a solution of dimethyl methylglucoside, in 10 per cent. hydrochloric acid, for twenty minutes under a condenser. During the hydrolysis, the specific rotation altered from 142.4° to the constant value -58.5°, and recalculation of the latter figure for the concentration of dimethyl glucose formed on hydrolysis gives +62.4°. This agrees with the equilibrium value subsequently found for the sugar, so that the reaction is quantitative.

After removal of the acid with barium carbonate, evaporation to dryness at 45°/15 mm., extraction with boiling acetone and concentration, a syrup was obtained which gradually deposited a

crop of minute prisms. The bulk of the sugar was, however, only obtained in the crystalline state after removal of the acetone and drying of the residue at 60°/15 mm. until constant in weight. Thereafter the compound was crystallised several times from dry ethyl acetate. Yield=63 per cent. of the weight of glucoside used:

Found, C=46.19; H=7.83; OMe=30.2.

$C_6H_{10}O_4(OMe)_2$  requires C=46.15; H=7.69; OMe=29.8 per cent.

By the process described above, dimethyl glucose was obtained in the form of minute prisms readily soluble in water, the lower alcohols, and acetone, sparingly soluble in ethyl acetate, insoluble in ether or hydrocarbon solvents. The melting point observed was very indefinite (70–105°), and this behaviour was shown to be due to the presence of the stereoisomeric  $\alpha$  and  $\beta$ -forms.

#### *$\beta$ -Dimethyl $\beta$ -Glucose.*

When the mixture of the  $\alpha$ - and  $\beta$ -isomerides was crystallised from solutions in ethyl acetate containing from 10 to 20 per cent. of the solute, the sugar separated in brittle, warty aggregates. The initial specific rotations of successive crops varied from +29° to 58°, and the melting points similarly ranged from 80° to 104°. No separation of the two forms could thus be carried out.

On the other hand, crystallisation from a dilute solution in ethyl acetate (not more than 5 per cent.) gave a crop of pointed prisms which showed a tendency to arrange themselves in clusters. With a solution of intermediate concentration (about 7 per cent.), the crop consisted partly of the prisms referred to above, and partly of opaque, spherical aggregates, which were easily distinguished from the prismatic crystals, and could be mechanically separated from them.

The prisms proved to be the  $\beta$  form of the sugar, and the spherical aggregates the  $\alpha$ -isomeride, but only the former could be obtained in quantity by crystallisation from ethyl acetate. In preparing the material used in the rotations, the concentration of the solution was limited to 5 per cent., and the uniformity of each crystalline crop was confirmed by microscopic examination. The  $\beta$ -isomeride thus isolated was practically pure, but melted indefinitely at about 100°. The final purification consisted in preparing a 30 per cent. solution of the sugar in anhydrous alcohol, and precipitating the dissolved material in two crops by the addition of dry ether. The first portion to separate melted at 108–110°, and consisted of the pure  $\beta$  form.



*Mutarotation of  $\beta$ -Dimethyl  $\beta$ -Glucose.*

Solvent.	c.	l.	Initial $\alpha_D^{20}$ .	Final $\alpha$ .	Initial $[\alpha]_D^{20}$ .	Final $[\alpha]_D^{20}$ .
Water .....	5.00	1	+0.53°	→ +3.22°	+10.60	→ +64.4°
Alcohol .....	5.02	2	0.57	→ 4.96	5.68	→ 49.41
Acetone .....	3.84	2	0.50	→ 3.91	6.52	→ 50.9

The speed with which equilibrium was attained in the three solvents differed in a marked degree. Thus, the aqueous solution assumed a constant rotation in about six hours. On the other hand, in alcoholic solution the change was exceedingly slow, while in acetone the sugar showed suspended mutarotation. In one experiment, in which anhydrous acetone, freshly prepared from the bisulphite compound, was used as a solvent, the alteration in specific rotation observed in fifteen days was only  $-6.5^\circ \rightarrow +8.2^\circ$ . The permanent value of  $-4.9^\circ$  was, however, reached in a few minutes on the addition of a catalyst. In each case, the curves representing the rotation changes were plotted, and, by extrapolation, the following initial values were indicated:

Solvent.	Water.	Alcohol.	Acetone.
$[\alpha]_D^{20}$	+5.7	+5.68°	-5.9

In the case of the alcoholic and acetone solutions, these values are, of course, very little removed from those determined experimentally.

 *$\beta$ -Dimethyl  $\alpha$ -Glucose.*

Nuclei of dimethyl  $\alpha$ -glucose were obtained, as described, by crystallisation of the equilibrium mixture of the sugar from 7 per cent. solutions in ethyl acetate. These nuclei proved of service in the following preparation of the  $\alpha$ -form of the sugar. A 30 per cent. solution of dimethyl  $\beta$ -glucose in ethyl alcohol was heated at  $100^\circ$  for thirty minutes so as to establish equilibrium. Sufficient dry ether was then added to precipitate about one-half of the dissolved material in the first crop. This fraction was essentially the pure  $\beta$ -form. The filtrate was further diluted with ether nucleated with the  $\alpha$ -isomeride, and preserved in a freezing mixture for two days, when a second crop, consisting of the  $\alpha$ -form, gradually separated. A third crop, which on microscopic examination appeared to be free from the prismatic  $\beta$ -form, was obtained on similarly nucleating the mother liquor.

$\beta$ -Dimethyl  $\alpha$ -glucose crystallises in dense spherical aggregates, which are quite opaque, so that no exact description of the crystalline form can be given. The crystals melted at  $85-87^\circ$ , and the compound showed downward mutarotation. Owing to the laborious nature of the separation of this isomeride, very little pure

material was obtained, and the mutarotation was only determined in acetone solution, so as to obtain an accurate value for the initial point. The change thus observed, for  $c=1$ , was  $\div 81.93^{\circ} \rightarrow 48.3^{\circ}$ .

*Proportion of  $\alpha$ - and  $\beta$ -Forms present in Equilibrium in Solution.*

The necessary data for the above calculation are only available where acetone was used as the solvent.

$$\begin{array}{lcl} \text{Initial } [\alpha]_D \text{ for } \alpha\text{-form} = \div 81.93^{\circ} & & \\ \text{,, ,, } \beta\text{-form} = \div 5.96^{\circ} & \text{Equilibrium } [\alpha]_D = 59.9^{\circ} & \end{array}$$

From these results, it will be seen that the equilibrium mixture contains 59 per cent. of the  $\alpha$ -form and 41 per cent. of the  $\beta$ -isomeride. Owing to lack of material, the rotation of the  $\alpha$ -form was not taken in aqueous solution, but it may be reasonably assumed that it does not differ notably from the value found in acetone solution. This is justified by the practical coincidence of the initial specific rotations of the  $\beta$ -form in these solvents, as determined by extrapolation. Further, the activity of dimethyl methylglucoside, which is an  $\alpha$ -form, is likewise unaffected by the nature of the solvent. The data for the calculation thus becomes:

$$\begin{array}{lcl} \text{Initial } [\alpha]_D \text{ for } \alpha\text{-form} = \div 81.93^{\circ} & & \\ \text{,, ,, } \beta\text{-form} = \div 5.7^{\circ} & \text{Equilibrium } [\alpha]_D = \div 24.4^{\circ} & \end{array}$$

This corresponds with a mixture consisting of 77 per cent. of the  $\alpha$ -form and 23 per cent. of the  $\beta$ -modification, values which are widely different from those found in the case of glucose.

*Effect of Heat in Altering the Equilibrium.*

On recovering the sugar from an aqueous solution, which had attained equilibrium, by evaporation of the solvent at  $36^{\circ}$  12 mm., the product showed practically no mutarotation. The equilibrium thus appears to be only slightly affected by change of concentration. A specimen of the sugar, isolated in the manner described above, was kept in the fused condition at  $120^{\circ}$  for an hour, after which, on dissolving the product in water, extensive upward mutarotation was observed. This treatment is known to alter equilibria in methylated sugars in the direction  $\alpha \rightarrow \beta$ , and the result thus justifies the stereochemical nomenclature we have applied to the two forms of this sugar.

*$\beta$ -Dimethyl Glucose phenylhydrazon.*

Several attempts were made to prepare an osazone from dimethyl glucose, but, although the process was modified in various ways, no sparingly soluble product was obtained, and the sugar was resimified.

Condensation with phenylhydrazine was, however, effected under the following conditions. A solution of the sugar (1 mol.), in an equal weight of water, was mixed with phenylhydrazine (3 mols.), and after thorough mixing, the liquid was preserved in the dark for six weeks in a sealed tube. A homogeneous syrup was thus obtained, which was dissolved in ether, the solution shaken successively with dilute acetic acid and water, dried over sodium sulphate, and evaporated. This treatment removed excess of the base, together with any free sugar. The product was a pale yellow syrup, which crystallised completely on keeping. No suitable recrystallising medium could be found, and the compound, which possessed the usual properties of a hydrazone, was analysed after heating gently in a vacuum until constant in weight:

Found,  $N=9.80$ .

$C_{14}H_{23}O_2N_2$  requires  $N=9.40$  per cent.

This nitrogen content is in itself sufficient proof that the compound is a hydrazone, and not an osazone. In a duplicate experiment, in which glucose was used, the sugar was completely converted into glucosephenylosazone.

Part of the expense of the foregoing investigations was defrayed by annual research grants received from the Carnegie Trust, for which the authors desire to express their indebtedness.

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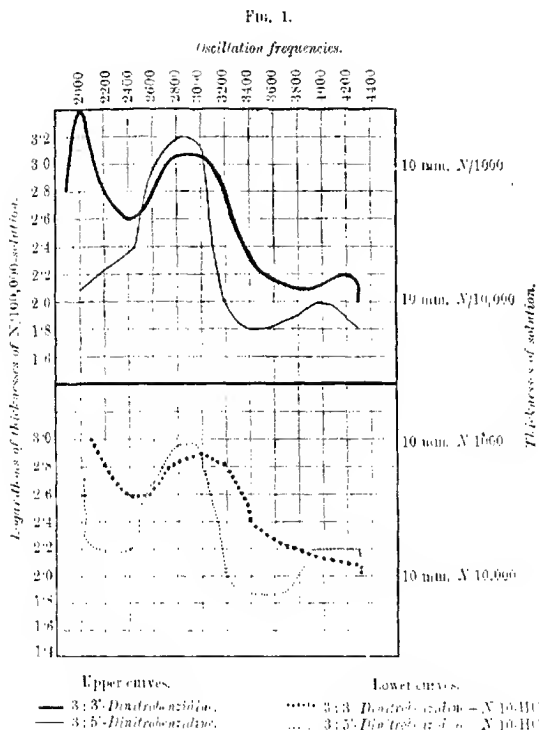
LXVI.—*Studies in the Diphenyl Series. Part IV.*  
*The Absorption Spectra of the Two Isomeric*  
*o-Dinitrobenzidines.*

By JOHN CANNELL CAIN, ALEXANDER KILLEN MACBETH, and  
ALFRED WALTER STEWART.

IN a previous communication by one of us in conjunction with Coulthard and Miss Micklethwait (T., 1912, **101**, 2298) it was shown that *o*-dinitrobenzidine exists in two isomeric forms, one being scarlet and melting at  $275^{\circ}$ , whilst the other is bright red and melts at  $233^{\circ}$ . In view of the interesting nature of this isomerism, it seemed of importance to bring all possible evidence to bear upon the point; and in the present communication the

description is given of the absorption spectra of the two compounds. For the sake of convenience in reference, we have adhered to the previous nomenclature, and describe the compounds as 3:3'-dinitrobenzidine and 3:5'-dinitrobenzidine respectively.

The absorption spectra of the two substances in alcohol are shown in the upper curves of Fig. 1. It will be seen that in the ultra-

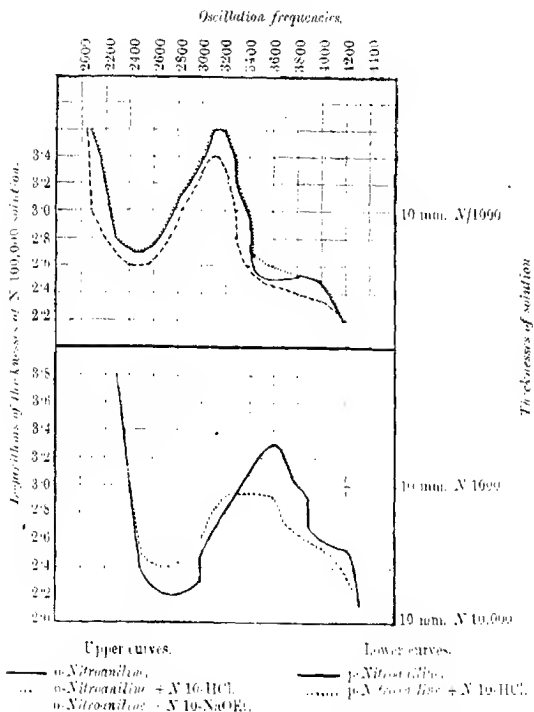


violet region the graphs resemble each other to a certain extent, both having a band in the region  $\lambda$  3100—3500. In the visible part of the spectrum the two curves differ considerably from one another, as in the curve for the 3:3'-compound there is a complete band the head of which lies about  $\lambda$  2400, whilst the graph for the 3:5'-compound shows the presence of a much deeper band, the

The compound which is most closely allied in structure to the dinitrobenzidines is *o*-nitroaniline, and we therefore photographed

its spectrum in alcoholic solution,\* and also in the presence of excess of hydrochloric acid and sodium ethoxide. The resulting graphs are shown in Fig. 3. A comparison of the curve of the pure substance with those of the dinitrobenzidines shows that there is a general resemblance between *o*-nitroaniline and the 3:3'-com-

FIG. 3.

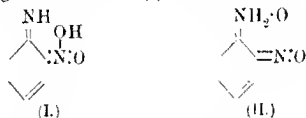


pound; but that the 3:5'-derivative differs from *o*-nitroaniline in the region 1700–2800, and also has a well-marked band at 3100–4000, where only a very shallow depression is shown in the *o*-nitroaniline spectrum. It is clear that if we can gain some

\* This had already been done by Morgan, Jølling, and Barnett (L. 1912, 101, 1213), the results being similar to ours.

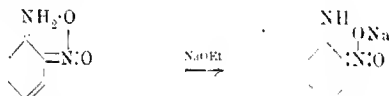
insight into the structure of the *o*-nitroaniline molecule it will aid us in our further consideration of the dinitrobenzidines, and this question must therefore now be considered.

An examination of the spectrum of *o*-nitroaniline shows that it has a band similar to those contained in the spectra of some quinones; and we are therefore justified in assuming that there is a quinonoid grouping in the *o*-nitroaniline molecule. This would lead us to assign the structure (I) to *o*-nitroaniline. At this point,



however, a new factor comes in; for the nitro-group is in the *aci*-form within active range of a basic radical. Interaction between these would take place, producing a substance of the structure (II). This formula resembles in some respects one which has been put forward by Meldola and Hollely (T., 1912, 101, 918) to account for the properties of picramic acid derivatives.

Before proceeding further, this idea must be tested so far as possible to see if it can be brought into agreement with other facts. By adding sodium ethoxide to a substance of this type it might be possible to convert it into the salt of a pseudo-acid having the structure shown below:



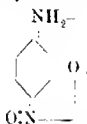
Now in order to do this it would be necessary to break a five-membered ring, which, as is well known, is a fairly stable type; and when this was done a substance would be obtained the quinonoid structure of which was unchanged in essential; thus we should expect to find very little change in the spectrum brought about by the addition of sodium ethoxide to the nitroaniline solution. The curves in Fig. 3 show that the experimental data agree with this.

A second test can be applied by studying the action of acid on the nitroaniline. The action in this case would be to open the ring and cause the substance to revert to the benzenoid form, an ordinary salt of the ammonium type being formed:



Examination of the curves shows that this does not take place.

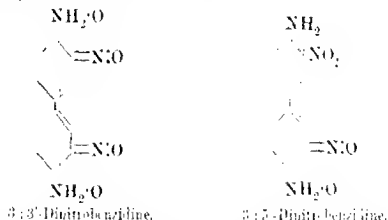
The substance retains its quinonoid character even in the presence of excess of acid. How can this be explained? We have already pointed out that the five-membered ring is a very stable type, and it seems likely that the action of the acid may not be sufficient to rupture it. In order to test this idea it is only necessary to substitute a less stable ring for the five-membered one; and a case in point is *p*-nitroaniline. Here the pure substance shows a band similar to that of *o*-nitroaniline, although much broader; so that the structure may be similarly written:



Now this internal salt contains a seven-membered ring instead of the five-membered one of *o*-nitroaniline; and such a seven-membered ring would, on general grounds, be less stable than the five-membered one. It will therefore be more easily ruptured by the action of acid, and the compound would tend to revert to the benzenoid structure to some extent and showing a less marked quinonoid band. The lower curves in Fig. 3 show that this holds good, for in this case the band obviously decreases in persistence in presence of acid.

This evidence justifies us in assuming that *o*-nitroaniline has the internal salt structure, and that, further, this ring is fairly stable in the presence of acid.

Let us now look at the benzidine derivatives in the light of this hypothesis. In their case we have to explain the occurrence of the substance in two isomeric forms, one of which is more closely allied to *o*-nitroaniline than the other. The formulæ below give one possible explanation of the difference:



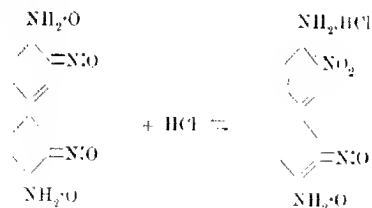
In the one formula both benzene nuclei are in the quinonoid form, whilst in the second there is one benzenoid and one quinonoid nucleus.



We must now apply a further series of tests to these formulae with the object of finding out whether they meet fresh requirements.

We have seen that in *o*-nitroaniline the five-membered ring is stable, to a great extent, in the presence of acid. From this we deduce that when acid is added to a solution of the diquinonoid benzidine derivative there would not be a marked change in the spectrum. A comparison of the curves in Fig. 1 will show that this corresponds with the experimental result; very little change in general character takes place when acid is added to the solution. On the other hand, in the case of the benzenoid-quinonoid compound there is a free amino-group which should unite with this acid and become saturated, thus giving a reversion towards the benzene spectrum. Let us take benzidine\* as a comparison substance. As can be seen from the lower curves in Fig. 2, the addition of hydrochloric acid to benzidine has the effect of shutting up the band and replacing it by a rapid extension of the spectrum. An examination of the curves of 3:5'-dinitrobenzidine alone and with hydrochloric acid present (Fig. 1) shows that a similar closing of the band takes place, although it is not so complete as in the case of benzidine, probably owing to the presence of the second nucleus in the quinonoid condition, which will be a disturbing factor; thus the hypothesis fits the facts very closely.

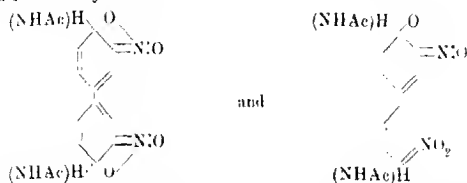
Attention should be drawn to the fact that hydrochloric acid is not quite without action in the case of 3:3'-dinitrobenzidine, although the alteration in the spectrum in this region is slight. The change may be ascribed to the tendency toward equilibrium between the two forms; in the presence of excess of acid a small amount of the ring compound would naturally tend to revert even in this case to the benzenoid type; but as can be seen from the curves, the amount of change which takes place is evidently very small:



Thus, from the spectroscopic point of view these formulae form a basis on which to explain the isomerism of the two *o*-dinitro-

\* Benzidine shows a slight deviation from Beer's law between  $N/10,000$  and  $N/100,000$  solutions. For the sake of simplicity, only the  $N/10,000$  curve is given.

compounds, and the existence of two *o*-dinitrophenyls, and of the acetyl derivatives of the *o*-dinitrobenzidines, can be accounted for in a similar way, thus:



It must be frankly stated, however, that spectroscopic evidence alone is not sufficient to decide a purely chemical question unless it is well supported by purely chemical data. In the present case the chemical evidence appears to favour the view put forward above, as it tends to show that the amino-groups are not perfectly normal in behaviour; for instance, the compounds do not readily form hydrochlorides as they would do if the amino-groups were free to react with acid, like the corresponding groups in benzidine.

The chief objection which can be brought against these formulæ is that it is difficult to understand why one form should not pass into the other; thus no change of either form is effected by treatment with sodium ethoxide. The stability of the five-membered ring when once formed would explain the non-conversion of the 3:3' compound into its isomeride; whilst it is well known that there is little inclination for benzenoid substances to revert to the quinonoid type, which would cover the case of the stability of the 3:5' substance.

#### *Conclusions.*

(1) The spectra of the two *o*-dinitrobenzidines show that there is a marked difference between the two substances.

(2) There is a resemblance in a certain degree between the spectrum of *o*-nitroaniline and that of 3:3' dinitrobenzidine.

(3) From the results obtained by studying the spectra of the *o*-dinitrobenzidines in the presence of acid and alkali, it appears probable that they differ from each other in the constitution of their benzene nuclei, the one compound containing two quinonoid rings, whilst the other is made up of a benzenoid and a quinonoid nucleus.

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LXVII.—*The Influence of the Constitution of Tertiary Bases on the Rate of Formation of Quaternary Ammonium Salts. Part I.*

By EBENEZER REES THOMAS.

THE investigations of Hofmann, Menschutkin, Bischoff, Wedekind, and others, have shown that the constitution of organic bases exercises a profound influence on their reactions with halogen compounds, but notwithstanding the attention which has been bestowed on the kinetics of these reactions, the velocity-constant measurements have dealt almost entirely with the effect of the constitution of the haloid on the course of the reaction.

N. Menschutkin (*Zeitsch. physikal. Chem.*, 1890, **5**, 589; **6**, 41; 1895, **17**, 193; 1900, **34**, 157; *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 46; 1902, **34**, 411; *Ber.*, 1895, **28**, 1398; 1897, **30**, 2775, 2966; 1905, **38**, 2465) has, however, carried out a complete investigation of a number of reactions of this type, studying not only the influence of the constitutions of both reagents, but also that of the solvent on the rate of reaction. In his work on the effect of the constitution of the base he dealt mainly with primary and secondary amines. The results which he obtained as to the influence of the constitution of tertiary bases will find further mention in this paper. Moore, Somervell, and Derry (T., 1912, **101**, 2459) show that some of Menschutkin's results are open to criticism on theoretical grounds. It is suggested that the experimental method described in the present communication might be expected to yield results of a higher degree of accuracy than those obtained by the method used by Menschutkin.

The velocity constants for the reaction between various aromatic tertiary bases and allyl bromide in *N*/10-absolute alcohol solution at 40.0° were determined. In some cases the constant for benzyl bromide was also measured.

It was found that with some compounds accurate results could only be obtained when the amount of quaternary ammonium bromide was estimated gravimetrically as silver bromide. This rendered the study of the very early stages of the reaction impracticable; but as in nearly every case the value of the constant remains the same over widely different periods, this is not of much consequence so far as the comparison of the rates is concerned. It was also found necessary to remove the unaltered haloid before precipitating the silver bromide, and this was done in every experiment. The latter precaution, if unnecessary for slowly reacting haloids, certainly cannot be neglected in the case of allyl bromide.

Wedekind (*Ber.*, 1899, **32**, 511; *Annalen*, 1901, **318**, 90) has extended the investigations in this field by studying the influence of the constitution of certain tertiary bases on quaternary ammonium salt formation. He determined the amount of salt formed at the end of a certain period of time under certain conditions, the estimation in each case being made by weighing the washed and dried product of the reaction.

It was considered advisable to carry out a systematic investigation of the actual velocity constants for various aromatic tertiary bases, under the conditions already described, in the hope that an exact measure might be made of the influence of the nature and position of the groups attached to the nitrogen atom.

The following results were obtained:

	Velocity constants		Ratio, Benzyl allyl
	Allyl bromide.	Benzyl bromide.	
Dimethylaniline .....	1.08	0.31	3.5
Methylethaniline .....	0.71		
Diethylaniline .....	0.094		
Methylpropylaniline .....	0.48		
Methylallylaniline .....	0.350		
Benzylmethylaniline .....	0.125		
Methylacetanilide .....	0.032	0.131	4.1
Benzylbenzylamine .....	0.8		
Dimethyl- <i>o</i> -toluidine .....	0.057	0.235	4.1
Dimethyl- <i>m</i> -toluidine .....	1.54		
Dimethyl- <i>p</i> -toluidine .....	2.59		
<i>p</i> -Bromo dimethylaniline .....	0.281	1.95	6.8
Dimethyl- <i>p</i> -aminobenzaldehyde .....	0.04		
Pyridine .....	0.43		
Quinoline .....	0.063		
<i>iso</i> Quinoline .....	0.185		
Methyltetrahydroquinoline .....	0.113		
Ethyltetrahydroquinoline .....	0.097		
2-Methylquinoline (quinoline) .....	0.035		
Methyltetrahydroquinoline .....	0.081		
Acetylpyridine .....	0.039	0.136	4.5

## EXPERIMENTAL.

### Purification of Materials.

The alcohol was purified by boiling rectified spirit over lime under a reflux condenser until all the lime was broken up, and subsequent distillation. This operation was repeated, and the alcohol then treated twice in a similar way with 1 per cent. of freshly turned calcium. The purity was finally tested by means of a velocity-constant determination. Rough preliminary experiments were generally carried out in rectified spirit solution, and it was found that the presence of water in the alcohol tends to accelerate the rate of reaction.

Pure allyl bromide was redistilled and kept in a desiccator protected from light.

It was distilled in small quantities as required, in order to obviate long keeping, whilst the velocity constant for each specimen was determined with a standard substance. In the case of one specimen of allyl bromide which was found to give rather low results, the rates for three standard bases were determined, and it was found that the ratio of the constants for the standard bromide to the constants for this bromide were 1.08, 1.07, 1.09 for methylallyl-aniline, *iso*quinoline, and methylethylaniline respectively (compare experiments 2 and 5). The constants for the bases which have been measured with this specimen of allyl bromide (called K') have therefore been multiplied by 1.08, so that all the numbers are strictly comparable.

The solid bases were all purified by recrystallisation, and in nearly every case of a liquid base a crystalline derivative was prepared and purified, from which the base was subsequently recovered. The quality of the numbers obtained was in each case taken as the final test of purity, so that purification was carried out until a good constant was obtained.

#### Method.

The reactions were carried out at 40° in glass-stoppered bottles, which were, as far as possible, protected from the action of light. Since only the comparative values of the constants are of importance, it was found most convenient to refer all data to concentrations at 15°.

*N/5*—Solutions of the base and of allyl bromide were therefore made up at 15° and placed in the 40° thermostat, together with the reaction-vessel. When the solutions (now a little less than *N/5*) had attained the temperature of the bath, equal quantities of the two solutions were in turn transferred to the reaction vessel by means of a pipette, the bottle being well shaken and the exact time of mixing noted.

At definite intervals of time, about 20 c.c.\* of the reaction mixture were transferred to a small separating funnel containing about 70 c.c. of about *N/10* to *N/20*-nitric acid (which at once arrested the reaction), and about 40 c.c. of light petroleum. After shaking and settling, nearly all the light petroleum was syphoned off, a second quantity of 30 c.c. being then added in order to remove any remaining traces of allyl bromide.

The aqueous layer was transferred to a small beaker, the light petroleum was washed twice with small quantities of water, and

\* The pipettes were calibrated so that the volume at 15° of the solution which they delivered at 40° was known.

the washings were added to the solution in the beaker. Silver nitrate solution was then added; the resulting precipitate was coagulated by stirring, and then collected, washed, dried, and weighed.

The results\* given below were calculated according to the usual formula for a bimolecular reaction:

$$K = \frac{1}{t} \frac{x}{a(a-x)},$$

$a$  and  $x$  being expressed as the number of gram-molecules per litre at 15°.

Column I gives time in hours elapsed since time of mixing; II, actual weight of silver bromide obtained; III,  $x$  calculated from II; IV, value of constant  $K$ . (As the maximum amount of iodide would give a decinormal solution, the numbers obtained by multiplying those in column III by 1000 express the percentage of salt formed.)

### Experiments with *Allyl Bromide*.

#### 1. *Dimethylaniline*.

A.	I.	II.	III.	IV.
	4.5	0.1186	0.03235	1.96
	5.5	0.1355	0.03715	1.97
	7.5	0.1628	0.04461	1.97
	8.8	0.1785	0.04893	1.99
	10.67	0.1975	0.05415	1.10

Mean  $K$  of  $A = 1.98$ .

Mean  $K$  of  $B = 1.05$ .

Mean of  $A$  and  $B = 1.05$ .

#### 2. (a) *Methylethylaniline*.

#### 2. (b) *Methylethylaniline*.

I.	II.	III.	IV.	I.	II.	III.	IV.
2.78	0.0570	0.0156	0.667	4.2	0.0550	0.0233	0.72
4.53	0.0843	0.0231	0.663	4.53	0.0600	0.0247	0.72
5.95	0.1017	0.0279	0.660	6.2	0.1130	0.0319	0.72
6.63	0.1115	0.03056	0.664				
7.25	0.1178	0.0323	0.658				

Mean  $K$  of  $A = 0.660$ .

Mean  $K$  of  $B = 0.661$ .

Mean of  $A$  and  $B = 0.6605$ .

$K = 0.6605 \times 1.08 = 0.713$ .

Mean  $K = 0.72$ .

Ratio  $K : K = 1.00$ .

\* In most cases, two determinations  $A$  and  $B$  were made, and the results of one determination are given in full.

## 3. Diethylylaniline.

I.	II.	III.	IV.
39.95	0.0790	0.02165	0.092
47.5	0.1091	0.0299	0.090
71.1	0.1450	0.03976	0.092
80.6	0.1580	0.04332	0.095
96.7	0.1765	0.0484	0.097

Mean  $K$  of  $A=0.093$ .Mean  $K$  of  $B=0.0955$ .Mean of  $A$  and  $B=0.094$ .(a) Methylallylaniline ( $K'$ ).

I.	II.	III.	IV.
7.8	0.0735	0.0215	0.323
10.3	0.0920	0.0252	0.327
11.2	0.0977	0.0268	0.327
12.08	0.1010	0.0285	0.330

Mean  $K'$  of  $A=0.327$ .Mean  $K'$  of  $B=0.322$ .Mean  $K'$  of  $A$  and  $B=0.324$ .Therefore mean  $K=0.324 \times 1.08$   
 $=0.350$ 

## 6. Methylbenzylaniline.

I.	II.	III.	IV.
21.00	0.0747	0.0205	0.123
27.37	0.0912	0.0250	0.122
27.4	0.1040	0.0285	0.122
43.3	0.1278	0.03505	0.124
46.43	0.1387	0.03665	0.1246

Mean  $K$  of  $A=0.123$ .Mean  $K$  of  $B=0.123$ .Mean of  $A$  and  $B=0.123$ .

## 8. Benzylideneaniline.

I.	II.	III.	IV.
2.8	0.0697	0.0191	0.835
3.83	0.0870	0.02355	0.818
4.7	0.0988	0.0271	0.791
5.27	0.1062	0.0292	0.781

Mean ( $K$ ) = 0.8.

## 10. Dimethyl-m-toluidine.

I.	II.	III.	IV.
2.47	0.0944	0.0250	1.11
3.72	0.1267	0.03175	1.13
4.82	0.1475	0.04045	1.11

Mean  $K'$  of  $A=1.12$ .Mean  $K'$  of  $B=1.13$ .Mean  $K$  of  $A$  and  $B=1.125$ .Therefore  $K=1.125 \times 1.08$   
 $=1.214$ .

## 4. Methylpropylaniline.

I.	II.	III.	IV.
7.92	0.1003	0.0275	0.479
9.42	0.1122	0.0308	0.472
11.0	0.1258	0.0345	0.479
13.53	0.1442	0.03955	0.483
21.07	0.1838	0.0504	0.482

Mean  $K$  of  $A=0.479$ .Mean  $K$  of  $B=0.480$ .Mean of  $A$  and  $B=0.480$ .5. (b) Methylallylaniline ( $K$ ).

I.	II.	III.	IV.
9.05	0.0878	0.0241	0.359
10.4	0.0972	0.02665	0.351
11.4	0.1042	0.02855	0.351
12.7	0.1123	0.0308	0.359
13.73	0.1190	0.0326	0.352

Mean  $K=0.350$ .Ratio:  $K/K'=0.350$   
 $0.324$  $=1.08$ .

## 7. Methylneetanilide.

I.	II.	III.	IV.
65.3	0.0630	0.0178	0.0329
88.4	0.0808	0.02215	0.0322
134.9	0.1123	0.0307	0.0322

Mean  $K$  of  $A=0.0323$ .Mean  $K$  of  $B=0.0322$ .Mean  $K$  of  $C=0.0314$ .Mean of  $A$ ,  $B$  and  $C=0.032$ .

## 9. Dimethyl-o-toluidine.

I.	II.	III.	IV.
47.66	0.0773	0.0212	0.0561
65.2	0.0969	0.02632	0.0538
95.5	0.1287	0.0353	0.0511
115.4	0.1488	0.0408	0.0497

Mean  $K$  of  $A=0.057$ .Mean  $K$  of  $B=0.057$ .Mean of  $A$  and  $B=0.057$ .

## 11. Dimethyl-p-toluidine.

I.	II.	III.	IV.
1.27	0.0992	0.0285	2.81
1.92	0.1304	0.0318	2.75
2.5	0.1538	0.0411	2.79
3.0	0.1719	0.0456	2.8
3.28	0.1788	0.0477	2.81

Mean  $K$  of  $A=2.80$ .Mean  $K$  of  $B=2.80$ .Mean of  $A$  and  $B=2.80$ .

12. *p-Bromodimethylamine.*

I.	II.	III.	IV.
9.45	0.0810	0.0222	0.302
12.78	0.1010	0.0277	0.300
16.60	0.1184	0.0325	0.290
19.66	0.1280	0.0351	0.275
22.79	0.1375	0.0377	0.266

Mean  $K'$  of  $A = 0.284$ .Mean  $K'$  of  $B = 0.282$ .Mean of  $A$  and  $B = 0.284$ .13. *p-Dimethylaminobenzaldehyde.*

I.	II.	III.	IV.
67.8	0.0852	0.02335	0.0450
87.6	0.1040	0.0255	0.0455
101.4	0.1078	0.0296	0.0460

Mean  $K' = 0.0455$ .14. *Pyridine.*

I.	II.	III.	IV.
9.92	0.1020	0.0250	0.392
12.35	0.1193	0.0327	0.394
15.95	0.1308	0.0355	0.401
15.66	0.1423	0.0390	0.408
18.17	0.1548	0.04245	0.406

Mean  $K' = 0.400$ . $K = 0.400 \times 1.08$ . $= 0.43$ .16. *Quinoline.*

I.	II.	III.	IV.
36.86	0.0638	0.0175	0.0574
60.81	0.0940	0.0203	0.0557
74.18	0.1094	0.0300	0.0578
85.14	0.1230	0.03372	0.0597

Mean  $K'$  of  $A = 0.0584$ .Mean  $K'$  of  $B = 0.0581$ .Mean  $K'$  of  $A$  and  $B = 0.0584$ .Therefore  $K = 0.0584 \times 1.08$   
 $= 0.063$ .15. *Methyltetrahydroquinoline.*

I.	II.	III.	IV.
19.75	0.0526	0.0144	0.085
42.6	0.0960	0.0263	0.084
47.83	0.1035	0.0284	0.083
52.0	0.1098	0.0301	0.083

Mean  $K' = 0.084$ .17. *isoQuinoline.*

I.	II.	III.	IV.
5.27	0.0692	0.01897	0.144
7.1	0.0913	0.02504	0.151
9.15	0.1055	0.02893	0.145
19.28	0.1150	0.03153	0.149

Mean  $K'$  of  $A = 0.147$ .Mean  $K'$  of  $B = 0.151$ .Mean  $K'$  of  $A$  and  $B = 0.149$ .Therefore  $K = 0.149 \times 1.08$   
 $= 0.161$ .18. *Methyltetrahydroquinoline.*

I.	II.	III.	IV.
1.1	0.1148	0.0315	0.414
5.9	0.1405	0.0385	0.417
8.27	0.1575	0.0432	0.416
20.51	0.1683	0.0461	0.417
33.25	0.1730	0.0491	0.415

Mean  $K'$  of  $A = 0.416$ .Mean  $K'$  of  $B = 0.410$ .Mean of  $A$  and  $B = 0.413$ .19. *Ethyltetrahydroquinoline.*

I.	II.	III.	IV.
42.2	0.0493	0.0135	0.0370
88.17	0.0900	0.0217	0.0372
94.5	0.0942	0.02583	0.0369
97.97	0.0972	0.02665	0.0371

Mean  $K' = 0.0370$ .



20. *2-Methylquinoline*  
(*Quinoline*).

I.	II.	III.	IV.
70.96	0.0680	0.01865	0.0323
95.6	0.0557	0.0285	0.0322
119.72	0.1021	0.0280	0.0325

Mean  $K$  of  $A = 0.0323$ .Mean  $K$  of  $B = 0.0325$ .Mean  $K$  of  $A$  and  $B = 0.0324$ .Therefore  $K = 0.0324 \times 1.08$   
 $= 0.0350$ .21. *Acetyl piperidine*.

I.	II.	III.	IV.
67.0	0.0617	0.0169	0.0304
86.9	0.0760	0.0209	0.0303
89.73	0.0783	0.0215	0.0305

Mean  $K = 0.0304$ .*Experiments with Benzyl Bromide.*22. *Dimethylaniline*.

I.	II.	III.	IV.
0.741	0.1172	0.03214	6.39
0.991	0.1407	0.03856	6.33
1.241	0.1605	0.044	6.33
1.49	0.1770	0.04853	6.325

Mean  $K$  of  $A = 6.34$ .Mean  $K$  of  $B = 6.35$ .Mean of  $A$  and  $B = 6.34$ .23. *Methylacetanilide*.

I.	II.	III.	IV.
15.68	0.0654	0.01745	0.132
20.43	0.0798	0.0213	0.132
25.68	0.0956	0.0255	0.133
27.33	0.1014	0.0271	0.136
36.5	0.1252	0.0334	0.137

Mean  $K = 0.134$ .24. *Dimethyl-*o*-toluidine*.

I.	II.	III.	IV.
12.5	0.0779	0.0212	0.215
15.6	0.0988	0.0257	0.222
21.65	0.1248	0.0312	0.241
35.0	0.1766	0.0484	0.268

Mean  $K$  of  $A = 0.24$ .Mean  $K$  of  $B = 0.23$ .Mean of  $A$  and  $B = 0.235$ .

A gradual rise in the constant is observed (compare Long, *loc. cit.*).

25. *p*-Bromodimethylaniline.

I.	II.	III.	IV.
2.38	0.1145	0.0314	1.92
3.08	0.1346	0.0369	1.90
3.65	0.1513	0.0415	1.94
4.52	0.1707	0.0468	1.95
5.21	0.1845	0.0506	1.96

Mean  $K = 1.93$ .26. *Acetyl piperidine*.

I.	II.	III.	IV.
21.92	0.0856	0.0229	0.135
25.75	0.0966	0.0258	0.135
29.58	0.1068	0.0285	0.135
32.75	0.1166	0.0311	0.138

Mean  $K$  of  $A = 0.136$ .Mean  $K$  of  $B = 0.137$ .Mean of  $A$  and  $B = 0.136$ .

It is hoped that further research on these lines may lead to exact general conclusions as to the mechanism of the reaction. At

the present stage of the work perhaps the following points may be noted.

1. The reaction-velocities for some of these bases have been determined under different conditions by other workers; Menshutkin measured the rates with allyl bromide (*a*) and methyl bromide (*b*) at 100° in benzene solution; Long (T., 1911, **99**, 2164) used *isoamyl* alcohol as solvent, and determined the rates with *isoamyl* bromide at 92.6°. The following is a comparative table of the results, the constant for pyridine being taken as 100:

	Long.	Menschutkin.		This paper.
		<i>a.</i>	<i>b.</i>	
<i>iso</i> Quinoline .....	—	130.0	112.0	113.0
Pyridine ..	100.0	100.0	100.0	100.0
Quinoline .....	12.3	10.5	18.6	14.7
2-Methylquinoline .....	2.7	—	4.0	8.9

Taking into consideration the great difference of the conditions and the effect of the solvent on the reaction (Menschutkin, *loc. cit.*, and Pinner and Franz, *Ber.*, 1905, **38**, 1539), the general agreement between the ratios is remarkable. It suggests that within certain limits the nature of the influence of the constitution on the rate of reaction is independent of the conditions.

2. Several good examples of "space-filling" by groups in proximity to the *N*-atom appear to be indicated, for example:

<i>o</i> -Dimethylaniline (1) .....	1.08	Diethylaniline (3) .....	0.094
Methylethylaniline (2) ...	0.71	Methylpropylaniline (4) .....	0.45
Benzylmethylaniline (6)...	0.123		

Here the influence of the position of the methyl group in (3) and (4) is analogous to the difference in the reactivity between methyl propyl ketone and diethyl ketone with various reagents, the numerical ratios being of much the same order of magnitude; whilst the differences between (1) and (2) agree in some measure with the differences between the reactivities of the analogous ketones. The benzyl group has, as might be expected, a larger hindering effect than the propyl group.

(*b*) The influence of a substituent in the ortho-position in relation to the *N*-atom is shown with:

Dimethylaniline (1) .....	1.08	<i>iso</i> Quinoline (17) .....	0.486
Dimethyl- <i>o</i> -toluidine (3) ..	0.057	Quinoline (18) .....	0.063

It may also be noted that whilst the ratio:

$$\frac{\text{methyltetrahydroquinoline}}{\text{quinoline}} = 6.5,$$

the ratio:

$$\frac{\text{methyltetrahydroquinoline}}{\text{quinoline}} = 2.3,$$

which may be explained if it is assumed that the steric hindrance of the methyl group attached to the nitrogen atom is increased by the presence of a substituent in the 2-position (compare dimethylaniline and diethylaniline).

3. It is evident, however, that although these effects are so marked, stereochemical influences are not the only factors of importance in the mechanism of this reaction. The constants:

Dimethylaniline .....	1.08	Dimethyl- <i>p</i> -toluidine.....	2.8
Methylacetanilide .....	0.032	<i>p</i> -Bromodimethylaniline .....	0.24
Dimethyl- <i>m</i> -toluidine .....	1.54	Dimethyl- <i>p</i> -aminobenzaldehyde	0.04

indicate what may perhaps be called the "polar" effect of the groups attached to the nitrogen atom. The amount of this effect seems to be comparable in a general way with the effect of the same grouping on the affinity constants of the tertiary bases, although the data in regard to the latter are somewhat scanty (compare Voley, T., 1908, **93**, 2122; Walker and Ashton, T., 1895, **67**, 576).

The ratios:

Quinoline .....	0.063	Quinaldine .....	0.001
Methyltetrahydroquinoline ...	0.110	Methyltetrahydroquinaldine...	0.003

seem to point to a similar conclusion.

It would appear, then, that an assumption of the existence of two influences—(a) stereochemical and (b) "polar"—is sufficient to explain all the present results.

The former appears to be much the larger factor of the two, and when both come into play is always dominant, for example:

(a) Dimethylaniline.....	1.08	Quinoline .....	0.063
(b) Diethylaniline .....	6.99	<i>iso</i> Quinoline .....	0.10
(c) Dimethyl- <i>o</i> -toluidine .....	0.057		

(b) and (c) are much stronger bases than (a), and quinoline is a stronger base than *iso*quinoline. Thus, although the influence of the polar factor would tend to make the numbers for (b) and (c) larger than that for (a), the stereochemical factor appears to be so great as to much more than neutralise this effect.

It must be noted, however, that Moore's results (*loc. cit.*) on the reactivity of primary, secondary, and tertiary aliphatic amines are not all capable of such simple explanation—the cases of ammonia and trimethylamine being anomalous.

The general effect of the stereochemical factor is, of course, easily explained according to modern views of steric hindrance. The effect of the "polar" factor on the course of the reaction is not clear, and it is hoped that further exact measurements of its effect may lead to a better understanding of the state of the bases in solution.

4. (a) It was thought possible that the presence of an ethylene linking in a group attached to the nitrogen atom might have an effect on the reactivity of the base. The results so far obtained indicate that such effect, if any, is very slight. Compare:

Methylpropylaniline.....	0.48
Methylallylaniline.....	0.35

In this connexion it is interesting to note that Wedekind and Paschke (*Ber.*, 1910, **43**, 1310) find that replacing the propyl group in phenylbenzylmethylpropylammonium iodide by an allyl group does not affect the rate of decomposition.

(b) The constant for benzyldeneaniline is not a satisfactory one; secondary decompositions undoubtedly occur, the odour of benzaldehyde being distinctly perceptible. At the same time, the numbers obtained, in view of their general similarity to those for dimethylaniline, etc., are in general accord with the formation of a quaternary ammonium compound containing a double bond attached to the nitrogen atom.

5. The exact significance of the constants for methylacetanilide and acetylpiperidine is perhaps not quite clear; but it is difficult to resist the conclusion that the bimolecular reaction which is being measured is the formation of the quaternary ammonium salt.

Wedekind states ("Stereochemie," 1907, p. 14) that methylacetanilide and methyl iodide do not combine with one another, although he observed (*Annalen*, 1901, **318**, 98) that some reaction does take place at about 250°, yielding a substance difficult to purify.

The only other evidence available on the formation of this type of compound was published recently by Dehn (*J. Amer. Chem. Soc.*, 1912, **34**, 1399) while the present investigation was in progress. This author has studied the action of acetyl chloride on tertiary bases in anhydrous ether solution; but although it would appear that pyridine acetyl chloride was obtained in a state of purity, it might be suggested that none of the other compounds was sufficiently pure to justify any definite conclusion as to its composition.

6. Owing to the fact that so many of the tertiary bases are liquids, and that the allied compounds which they are likely to contain as impurities are very similar in physical constants, it is often difficult to obtain a simple criterion of purity. It is suggested that a measurement of the reaction-velocity with allyl bromide, in view of the accuracy possible, the convenience of the conditions, and the small amount of material required, will supply the best criterion for purity of tertiary bases.

In conclusion, the author desires to acknowledge the assistance which he received from the late Dr. H. O. Jones, F.R.S., who suggested the investigation of this problem, and also to thank Prof. W. J. Pope, F.R.S., for his advice and encouragement.

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LXVIII.—*Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. Part I. Resolution of Phenylmethylethyl-azonium Iodide into Optically Active Components.*

By BAWA KARTAR SINGH.

LEBEL first suggested that quaternary ammonium salts containing no asymmetric atom other than one of quinquevalent nitrogen could exist in optically active modifications (*Compt. rend.*, 1891, **112**, 724), but the experimental evidence upon which the view was based is now known to be erroneous (Pope and Read, *T.*, 1912, **101**, 519). The first definite case of the existence of stereoisomerism of the kind indicated was described by Pope and Peachey (*T.*, 1893, **75**, 1127), and consisted in the resolution of phenylbenzylmethylallylammonium iodide into optically active isomerides. A number of quaternary ammonium compounds have since been resolved by the method of Pope and Peachey.

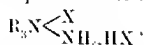
In the present paper the resolution of a member of another type of enantiomorphous compound, namely, an asymmetric azonium iodide, is described; the work was undertaken at the suggestion of the late Dr. H. O. Jones.

The quaternary azonium compounds have the general formula  $R_1R_2R_3XX\cdot NH_2$ , in which X represents a halogen atom, and in them also the optical activity is associated with the presence of an asymmetric nitrogen atom. Besides the fact that such compounds are capable of resolution, as was to be expected from theoretical considerations, some other interesting points have arisen from the present investigation; these are chiefly concerned with the difference in the latent additive activity of the two nitrogen atoms when they are directly linked, as in the case of the compounds under examination, and when they are separated by a sufficiently long chain of other groups. To explain such differences a simple hypothesis is developed.

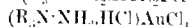
The azonium compounds examined were produced by the action of alkyl iodides on unsymmetrical disubstituted hydrazines in two different ways, and the same compounds resulted in each case. This, therefore, disposes of the view put forward by LeBel (*Compt. rend.*, 1899, **129**, 548) that the order in which an alkyl group is introduced is material, and establishes that no isomerides other than the two optical antipodes are formed in this way. This is an important fact, as it has bearing on the question of configuration of quinquivalent nitrogen, about which, however, much uncertainty still prevails.

The observations on the action of alkyl iodides on unsymmetrical disubstituted hydrazines, which are recorded below, have made clear that the union of the alkyl iodide takes place at the  $\alpha$ , and not the  $\beta$ , nitrogen atom, since when the order of introduction of the alkyl group is varied, the same end-product results. This is quite in harmony with the observations of Harries and Haga (*Ber.*, 1898, **31**, 56) on the direct action of alkyl iodides on hydrazine hydrate, in which it has been shown that the alkyl groups attach themselves only to one of the two nitrogen atoms, producing compounds of the type  $\begin{smallmatrix} \text{N} \cdot \text{R} \cdot \text{H} \\ | \\ \text{N} \cdot \text{H}_2 \end{smallmatrix}$ ,  $\begin{smallmatrix} \text{N} \cdot \text{R}_2 \\ | \\ \text{N} \cdot \text{H}_2 \end{smallmatrix}$ , and finally  $\begin{smallmatrix} \text{N} \cdot \text{R} \cdot \text{I} \\ | \\ \text{N} \cdot \text{H}_2 \end{smallmatrix}$ .

These observations may be explained by the hypothesis that it is not possible for both the nitrogen atoms to become quinquivalent at the same time owing to steric interference or hindrance. Hydrazine dihydrochloride,  $\begin{smallmatrix} \text{N} \cdot \text{H}_2 \cdot \text{Cl} \\ | \\ \text{N} \cdot \text{H}_2 \cdot \text{Cl} \end{smallmatrix}$ , is, however, known, but here the possibility of steric hindrance does not occur. Some experimental evidence is available which may be adduced in favour of this hypothesis. It might be expected that the free amino-group in the azonium compounds,  $\text{R}_3\text{N} \cdot \begin{smallmatrix} \text{X} \\ | \\ \text{N} \cdot \text{H}_2 \end{smallmatrix}$ , would react with acids ( $\text{HX}_1$ ) to yield salts, but all attempts to isolate salts of the type



were unsuccessful. Furthermore, the platinum and the aurichlorides of the general formulae  $(\text{R}_3\text{N} \cdot \text{N} \cdot \text{H}_2 \cdot \text{HCl})_2\text{PtCl}_6$  and



respectively are not produced, the compounds which are obtained containing the free amino-group, namely,  $(\text{R}_3\text{N} \cdot \text{N} \cdot \text{H}_2)_2\text{PtCl}_6$  and  $(\text{R}_3\text{N} \cdot \text{N} \cdot \text{H}_2)_2\text{AuCl}_4$ .

This behaviour is again in harmony with the platinumchloride of hydrazine itself, namely,  $(\text{N} \cdot \text{H}_2 \cdot \text{N} \cdot \text{H}_2)_2\text{PtCl}_6$ , and of other disubstituted hydrazines. It has also been shown that the non-basic character of the amino-group is the result of the quinquivalency of the

adjacent nitrogen atom, for it has been found that phenyltrimethylhydrazine hydrochloride,  $C_6H_5 \cdot N(C_2H_5) \cdot NH_2 \cdot HCl$ , does not combine with methyl iodide, whereas the free base reacts with methyl iodide to give the azonium compound,  $C_6H_5 \cdot N(C_2H_5)(CH_3)(NH_2)I$ .

Harries has further shown (*Ber.*, 1894, 27, 702) that by the action of methyl iodide on phenyldimethylhydrazine, phenyltrimethylazonium iodide,  $C_6H_5 \cdot N(CH_3)_3I \cdot NH \cdot CH_3$ , is produced, and it has also been found (compare Meyer and Jacobson, "Organ. Chemie," Band II., p. 311) that by the action of methyl iodide on phenyltrimethylhydrazine,  $C_6H_5 \cdot N(CH_3) \cdot N(CH_3)_2$ , in which both the nitrogen atoms are tertiary, the diquaternary azonium compound is not produced. The case is, however, different when the two nitrogen atoms are not directly linked, but are separated by a sufficiently long chain of methylene groups; both of them can then become quinquivalent at the same time, as in the cases of the ethylenedikairolinium diiodides (*Ber.*, 1903, 36, 1163) and trimethylenebisphenylmethylethylammonium iodide (*Ber.*, 1916, 43, 2707). The fact that the trimethylene diquaternary ammonium compounds, in which the nitrogen atoms are further apart, are much more readily formed than the ethylene diquaternary ammonium compounds, is additional evidence in support of the hypothesis suggested. Although the facts cited seem to be sufficient to warrant the above view, it is intended to subject it to a further experimental study.

The resolution of phenylmethylethylazonium iodide was effected by the aid of several optically active acids. The *d*-camphor- $\beta$ -sulphonate of the base was prepared by boiling a mixture, in equivalent proportions, of the azonium iodide and the silver salt with ethyl acetate (Pope and Peachey's method). The hydrogen *d*-tartrate and the hydrogen *d*-camphorate were prepared by half neutralising the azonium hydroxide with the corresponding acids. From what has been already said, it is clear that the acid radicle in these salts takes the place of the iodine of the iodide or the hydroxyl group of the hydroxide. In all the three cases examined, the less soluble salt which separates out on fractional crystallisation contains the *l*-base. The *d*-camphor- $\beta$ -sulphonate gives the maximum molecular rotatory power for the *l*-phenylmethylethylazonium ion,  $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N^+$ , as  $[M]_D$  about  $-16^\circ$ , the hydrogen *d*-tartrate as about  $-30^\circ$ , and the hydrogen *d*-camphorate as about  $-6^\circ$ .

The low values obtained for the molecular rotatory powers for the optically active ion,  $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N^+$ , are rather noteworthy. For the sake of comparison, the value of  $[M]_D$  for  $(C_6H_5)(C_2H_5)(CH_3)NCl \cdot OH$ ,  $41^\circ$  (J. Meisenheimer, *Ber.*, 1908, 41,

66), and that for  $(C_6H_5)(C_2H_5)(CH_3)(C_7H_7)NI$ ,  $64.4^\circ$  (Wedekind and Fröhlich, *Ber.*, 1906, **39**, 4437), may be cited, but this comparison is of little value as the molecular rotatory power is so greatly influenced by the chemical constitution of the compound.

Autoracemisation occurs in the case of these compounds; it takes place rapidly in the case of phenylmethylethylazonium *d*-camphor-niphonate, the aqueous solution becoming partly racemic within twenty-four hours. In the case of the hydrogen *d*-tartrate the inversion occurs very slowly; the active *l*-avo-iodide which is obtained from the hydrogen *d*-tartrate also undergoes a partial racemisation on keeping in alcoholic solution. The hydrogen *d*-camphorate, which is very slowly resolved, racemises within twenty hours of making up the aqueous solution.

#### EXPERIMENTAL.

Phenylethylhydrazine,  $C_6H_5 \cdot N(C_2H_5) \cdot NH_2$ , is obtained by dissolving sodium in the calculated quantity of phenylhydrazine contained in a distillation flask, distilling off the aniline and any excess of phenylhydrazine at  $180^\circ$  under diminished pressure, and treating the resulting sodium phenylhydrazine with ethyl iodide (Michaelis, *Ber.*, 1898, **30**, 2810). The phenylethylhydrazine is purified by conversion into its hydrochloride; this melts at  $146-147^\circ$ , and not at  $137^\circ$ , as stated by Michaelis. (Found, Cl = 20.78. Calc., Cl = 20.58 per cent.)

#### Phenylmethylethylazonium Iodide, $(C_6H_5)(C_2H_5)(CH_3)(NH_2)NI$ .

This substance was prepared by two methods: (a) *By the action of methyl iodide on phenylethylhydrazine.*—Phenylethylhydrazine hydrochloride (43.1 grams) was treated with potassium hydroxide, the liberated base extracted with ether, the solution dried over potassium hydroxide, and most of the ether evaporated off; one molecular proportion of methyl iodide (35.5 grams) was then added, and the mixture cooled in ice. On the addition of a little ether, white crystals began to appear, and the whole set to a solid cake in the course of two days. The crude product (53 grams) melted at  $114-115^\circ$ , and was recrystallised from hot alcohol; the purified azonium iodide melted and decomposed at  $119^\circ$ . The cooling mentioned is necessary, and if omitted, the yield becomes poor, and a dark coloured product results. The azonium iodide is soluble in water, less so in alcohol, somewhat soluble in hot chloroform, and insoluble in benzene or ether. On keeping for some time it turns blue, but the melting point remains unchanged.

(b) *By the action of ethyl iodide on phenylmethylethylhydrazine.*—



Phenylmethylhydrazine (10.3 grams) was mixed with one molecular proportion of ethyl iodide (13.2 grams); the mixture was cooled in ice, and on the addition of a little ether a white turbidity was produced, which on rubbing became crystalline. After three days the crystalline product was collected, washed with ether, and dried in a vacuum desiccator. The crude product (11.8 grams) melted and decomposed at 106–108°, and was recrystallised from hot alcohol; the purified azonium iodide melted at 119° with decomposition. A mixture of the azonium iodides obtained by the two different methods gave the same melting point; the first method of preparation gave much the better yield:

0.14385 gave 0.2047 CO<sub>2</sub> and 0.0725 H<sub>2</sub>O. C = 38.81; H = 5.6.

0.1517 „ 13.65 c.c. N<sub>2</sub> (moist) at 28.2° and 758 mm. N = 9.9.

0.2747 „ 0.2313 AgI. I = 45.48.

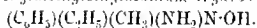
0.2858 „ 0.2420 AgI. I = 45.76.

C<sub>9</sub>H<sub>15</sub>N<sub>2</sub>I requires C = 38.84; H = 5.45; N = 10.1; I = 45.61 per cent.

*Action of Methyl Iodide on Phenylethylhydrazine Hydrochloride.*

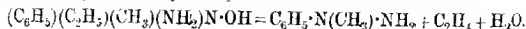
Phenylethylhydrazine hydrochloride (2 grams), dissolved in chloroform, was mixed with methyl iodide (2 grams). The mixture was at first cooled in ice, and was afterwards allowed to remain at the ordinary temperature for three days without any crystals appearing; on evaporation on the water-bath, practically all the phenylethylhydrazine hydrochloride used, melting at 147°, was recovered; thus, no combination occurs between methyl iodide and phenylethylhydrazine hydrochloride, whilst the azonium compound is formed if the free base is mixed with methyl iodide under similar conditions.

*Phenylmethylethylazonium Hydroxide,*



This substance is prepared by the action of moist silver oxide on an aqueous solution of phenylmethylethylazonium iodide. The mixture is agitated vigorously for some time at the ordinary temperature, and after filtration, a strongly alkaline aqueous solution of the hydroxide is obtained. The hydroxide is obtained as a colourless syrup, which does not crystallise on allowing the solution to evaporate spontaneously in a vacuum desiccator; on keeping for some time it becomes coloured, with slow production of minute gas bubbles.

On heating the syrupy hydroxide in an oil-bath up to 130°, it decomposes with evolution of ethylene; water is also produced, and the decomposition may be represented thus:



It is to be noted that the methyl group does not split off, as is generally the case, but remains attached to the nitrogen atom. The residual oil is strongly alkaline, and attempts made to identify phenylmethylhydrazine as its acetyl derivative were unsuccessful; it is inferred that the secondary hydrazine produced undergoes further decomposition.

The subject was not pursued further owing to lack of material.

*Phenylmethylethylazonium  $\alpha$ -Camphor- $\beta$ -sulphonate,*  
 $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N \cdot SO_3 \cdot C_{10}H_{17}O.$

The finely powdered azonium iodide (15 grams) was added in small quantities at a time to one molecular proportion of finely powdered silver  $\alpha$ -camphor- $\beta$ -sulphonate dissolved in boiling ethyl acetate moistened with a few drops of water on the water-bath. The contents of the flask were kept shaken, and after the addition of the whole of the iodide heating was continued for another half-hour to complete the reaction. The ethyl acetate was then distilled off, and the solid residue consisting of the azonium camphorsulphonate and silver iodide transferred to a Soxhlet apparatus and extracted with ethyl acetate until only silver iodide remained behind. The crude camphorsulphonate (17 grams) obtained in this way melted at  $133-134^\circ$ , and after being again extracted with acetone and crystallised, it melted at  $134-135^\circ$ :

0.1200 gave 0.2640  $CO_2$  and 0.0853  $H_2O$ .  $C=59.99$ ;  $H=7.9$ .

$C_{15}H_{20}O_4N_2S$  requires  $C=59.69$ ;  $H=7.85$  per cent.

The camphorsulphonate was crystallised several times from acetone, and its rotatory power determined, with the following result:

0.3334 gram, made up to 21.1 c.c. with water, gave, in a 2-dm. tube at  $28^\circ$ ,  $\alpha_D + 0.295^\circ$ , whence  $[\alpha]_D = 9.34^\circ$  and  $[M]_D = 35.7^\circ$ .

The observations were made thirty minutes after solution.

The molecular rotatory power of the  $\alpha$ -camphorsulphonic ion is  $[M]_D + 51^\circ$ , whence the basic ion has approximately  $[M]_D - 15.3^\circ$ . On preservation, the rotatory power of the solution gradually increased until after twenty-four hours the constant value  $[M]_D + 52^\circ$  was attained.

Determinations of rotatory power made with another sample independently prepared and fractionally recrystallised from a mixture of acetone and ethyl acetate gave the following result:

0.4385 gram, made up to 20.2 c.c. with water, gave  $\alpha_D + 0.425^\circ$  in a 2-dm. tube at  $29^\circ$ , whence  $[\alpha]_D + 9.79^\circ$  and  $[M]_D + 37.4^\circ$ .

The observation was made fifteen minutes after solution, and after

twenty-five minutes the value  $[M]_D +41.45^\circ$  was obtained. The rotatory power became constant at the value for the acid ion within twenty-four hours.

*Phenylmethylethylazonium Platinichloride,*  
 $[(C_6H_5)(C_2H_5)(CH_3)(NH_2)N]_2PtCl_6$ .

On adding platonic chloride solution to a concentrated aqueous solution of the above camphorsulphonate, acidified with concentrated hydrochloric acid, an orange-coloured, crystalline substance separates. On crystallisation from hot water containing hydrochloric acid it is obtained in arborescent, orange-coloured needles, melting and decomposing at  $159^\circ$ . On keeping for some time the salt becomes dark brown, and the melting point falls:

0.1221 gave 0.0333 Pt. Pt=27.27.

$C_{18}H_{30}N_4Cl_6Pt$  requires Pt=27.46 per cent.

*Phenylmethylethylazonium Aurichloride,*  
 $[(C_6H_5)(C_2H_5)(CH_3)(NH_2)N]AuCl_4$ .

On the addition of gold chloride in hydrochloric acid solution to a strong aqueous solution of the above camphorsulphonate, a yellow, crystalline substance is precipitated; this is practically insoluble in cold water, but moderately so in hot water, from which solvent, in the presence of hydrochloric acid, it crystallises in golden-yellow, stout prisms, melting and decomposing at  $97^\circ$ . This salt also changes colour on keeping, turning into a deep violet, hygroscopic substance:

0.1606 gave 0.06465 Au. Au=40.26.

$C_9H_{15}N_2Cl_4Au$  requires Au=40.23 per cent.

*Phenylmethylethylazonium Hydrogen  $\alpha$ -Tartrate,*  
 $(C_6H_5)(C_2H_5)(CH_3)(NH_2)N \cdot C_4H_6O_6$ .

One molecular proportion of phenylmethylethylazonium iodide is dissolved in alcohol, the solution agitated with a slight excess of the calculated quantity of moist silver oxide for some time at the ordinary temperature, and then filtered into an alcoholic solution containing one molecular proportion of tartaric acid. The alcoholic filtrate is concentrated on the water-bath, and then treated with ether until a white turbidity is produced; this on being rubbed becomes crystalline. The solid substance is purified by recrystallisation from alcohol, and forms colourless, thin prisms, which melt at about  $80^\circ$  to a viscid liquid:

0.14375 gave 0.2555  $\text{CO}_2$  and 0.0934  $\text{H}_2\text{O}$ .  $\text{C}=48.82$ ;  $\text{H}=7.27$ .

0.1178 „ 0.25 c.c.  $\text{N}_2$  (moist) at  $24^\circ$  and 761.2 mm.  $\text{N}=8.81$ .

$\text{C}_{30}\text{H}_{20}\text{O}_6\text{N}_2$  requires  $\text{C}=52.00$ ;  $\text{H}=6.66$ ;  $\text{N}=9.33$  per cent.

$\text{C}_{30}\text{H}_{20}\text{O}_6\text{N}_2 \cdot 1\text{H}_2\text{O}$  requires  $\text{C}=49.05$ ;  $\text{H}=6.92$ ;  $\text{N}=8.80$  per cent.

The salt thus appears to contain one molecule of water of crystallisation.

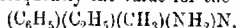
The hydrogen *d*-tartrate was recrystallised from a mixture of alcohol and ether, and a determination of its rotatory power gave the following results:

0.5072 gram, made up to 22 c.c. with water, gave, in a 2-dcm. tube at  $25^\circ$ ,  $\alpha_D +0.59^\circ$ , whence  $[\alpha]_D +12.8^\circ$  and  $[\text{M}]_D +40.7^\circ$ .

After several more crystallisations the following value was obtained:

0.4498 gram, made up to 20.95 c.c. with water, gave, in a 2-dcm. tube at  $30^\circ$ ,  $\alpha_D +0.16^\circ$ , whence  $[\alpha]_D +7.21^\circ$  and  $[\text{M}]_D +22.9^\circ$ .

The mean value for the hydrogen tartrate ion,  $\text{C}_4\text{H}_4\text{O}_6\text{II}^-$ , is  $[\text{M}]_D +42^\circ$ , and consequently the value for the basic ion,



$[\text{M}]_D -30^\circ$  approximately.

The results of rotatory-power determinations made with a sample repared independently and fractionally recrystallised from a mixture of alcohol and ether gave the following results. The substance was dissolved in water, and made up to 19.9 c.c. at  $23^\circ$ . The rotatory-power determinations were carried out in a 2-dcm. tube, and the observations were made about thirty minutes after making up the solution:

1st recrystallisation:			
0.2845 gram substance .....	$+0.377^\circ$	$-13.25^\circ$	$+42.1^\circ$
2nd recrystallisation:			
0.5113 gram substance .....	$+0.519^\circ$	$+10.15$	$+32.3^\circ$
3rd recrystallisation:			
0.4194 gram substance .....	$+0.396^\circ$	$+9.42^\circ$	$-39.6^\circ$
after 34 hours .....	0.42	9.98	31.7
„ 21 „ .....	0.423	10.0	31.8
„ 28 „ .....	0.40	9.49	30.2
Final recrystallisation:			
0.3662 gram substance .....	$+0.259^\circ$	$-7.04^\circ$	$+22.4^\circ$
after 25 hours .....	0.276	7.5	23.9

The values of  $[\text{M}]_D$  given above are calculated for the composition  $\frac{1}{2}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2, \text{H}_2\text{O})$ .

*1-Phenylmethylethylgluzonium Iodide.*

This salt was precipitated in very minute crystals when the solution of the above tartrate (having  $[\text{M}]_D + 22.4^\circ$ ) was rendered faintly alkaline with sodium carbonate solution, and then treated with solid potassium iodide. It was recrystallised from a mixture of alcohol and ether, and melted and decomposed at  $115\text{--}116^\circ$ :

0.1161 gram, made up in alcohol to 12 c.c., gave, in a 1-dm. tube at  $24^\circ$ ,  $\alpha_D - 0.05^\circ$ , whence  $[\alpha]_D - 5.2^\circ$  and  $[\text{M}]_D - 14.4^\circ$ .

The observations were made about thirty minutes after solution. After forty-two hours the values obtained were  $\alpha - 0.05^\circ$ ,  $[\alpha]_D - 3.1^\circ$ , and  $[\text{M}]_D - 8.6^\circ$ . Some racemisation thus occurs with the active iodide in alcoholic solution.

*Phenylmethylethylgluzonium Hydrogen d-Camphorate,*  
 $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)(\text{CH}_3)(\text{NH}_2)\text{N}\cdot\text{C}_{10}\text{H}_{15}\text{O}_4$ .

One molecular proportion of the azonium iodide was dissolved in alcohol, and treated with a slight excess of moist silver oxide at the ordinary temperature. After being thoroughly agitated for some time it was filtered into an alcoholic solution containing one molecular proportion of *d*-camphoric acid. The resulting solution was evaporated on the water-bath as far as possible, a turbid liquid containing a little metallic silver being thus obtained, which was again filtered. On the addition of ether an oil separates, which, after remaining for a few hours, deposited a considerable quantity of colourless, prismatic crystals. The oily matter was again dissolved in alcohol with the addition of sufficient ether to produce the white turbidity, and on allowing to remain for some time it became crystalline. On recrystallisation from hot alcohol the salt was obtained in rhombic plates, melting and decomposing at  $178\text{--}179^\circ$ . For analysis, the salt was dried in the steam-oven:

0.1335 gave 0.3162  $\text{CO}_2$  and 0.1010  $\text{H}_2\text{O}$ .  $\text{C} = 64.6$ ;  $\text{H} = 8.41$ .

$\text{C}_{19}\text{H}_{29}\text{O}_4\text{N}_2$  requires  $\text{C} = 65.14$ ;  $\text{H} = 8.57$  per cent.

The rotatory power of the salt decreases very slowly with successive crystallisations, and becomes constant after about seven recrystallisations. In the following determinations the substance was dissolved in water, made up to 19.9 c.c., and examined in a 2-dm. tube at  $23^\circ$  about thirty minutes after making up the solution:

1st recrystallisation :	$\alpha$	$[\alpha]_D$	$[\eta]_D$
0.1608 gram substance .....	+ 0.275°	+ 17.0°	+ 59.6°
2nd recrystallisation :			
0.2046 gram substance .....	+ 0.327°	+ 15.9°	+ 55.7°
4th recrystallisation :	$\alpha_D$		
0.2865 gram substance .....	+ 0.468°	+ 16.25°	+ 56.9°
5th recrystallisation :			
0.2218 gram substance .....	+ 0.362°	+ 16.24°	+ 56.8°
7th recrystallisation :			
0.1256 gram substance .....	+ 0.199°	+ 15.77°	+ 55.2°
after 20 hours .....	0.219	17.35	60.7

The mean value for the acid camphoric ion,  $C_{10}H_{14}O_4H^-$ , is  $[M]_D + 61.4^\circ$  (Everatt, T., 1908, **93**, 1233), and consequently the mean value for the basic ion is about  $[M]_D - 6.2^\circ$ .

Most of the rotatory-power determinations were carried out with the Landolt-Lippich triple-field polarimeter purchased out of a special grant made by the late Eastern Bengal and Assam Government, of which grateful acknowledgment is made here. I have also much pleasure in thanking my friend and colleague, Mr. E. R. Watson, for the kindly treatment and encouragement in my work which I have received from him.

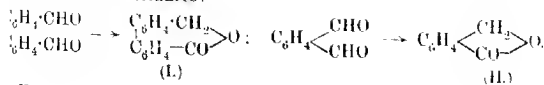
The further study of this and other azonium iodides is in progress.

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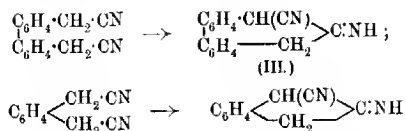
## LXIX.—The Formation of Cyclic Compounds from Derivatives of 2 : 2'-Ditolyl.

By JAMES KENNER.

From an earlier paper (Kenner and Turner, T., 1911, **99**, 2101) it appeared that a close relationship existed between the derivatives of 2 : 2'-ditolyl and those of *o*-xylene. Thus, 2 : 2'-dialdehydodiphenyl underwent condensation in presence of alkali hydroxide with the production of an  $\epsilon$ -lactone (I), a reaction which was exactly analogous to the production of phthalide (II) from *o*-phthalaldehyde in similar circumstances:



Further, the formation of 1-imino-2-cyano-3:5-dibenzo- $\Delta^{3:5}$ -*cycloheptadiene* (III) from  $\omega\omega'$ -dicyano-2:2'-ditolyl under the influence of sodium ethoxide corresponded with the reaction observed by Moore and Thorpe (T., 1908, 93, 165) in the case of *o*-xylylene dicyanide:

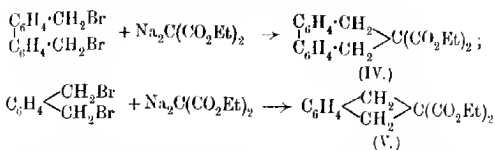


These observations, coupled with the formation of an anhydride and an imide from diphenic acid, led to the suggestion that the 2:2'-position in diphenyl derivatives is an effective ortho-position, and that the seven-membered doubly unsaturated rings produced in the above reactions are more closely allied to saturated *cyclopentane* derivatives than to those of *cycloheptane*.

These views have received important support from the fact (since communicated to the author by Dr. J. F. Thorpe) that it is not possible to synthesise derivatives of *cyclohexane* from  $\alpha\epsilon$ -dicyanopentane under the conditions of the imino-condensation just mentioned. The reaction therefore constitutes a sensitive test of the proximity of the  $\omega$ -cyanogen and the 1-methylene radicals in such compounds—as, indeed, would be expected in view of the entire absence of “constraint” from the conditions under which the reaction is carried out.

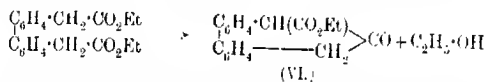
The experiments now to be described were undertaken in order to accumulate further evidence in connexion with the synthesis of cyclic compounds from derivatives of 2:2'-ditolyl, and as a result it may be said that the relationship indicated above is completely established, so far as the formation of seven-membered rings is concerned. Further, an illustration is supplied of the fact that, contrary to the opinion so widely entertained, the mere number of carbon atoms may not be the most important factor in determining whether ring formation can or can not take place.

In the first place, it was shown that  $\omega\omega'$ -dibromo-2:2'-ditolyl condenses with ethyl malonate in presence of sodium ethoxide with the production of *diethyl 3:5-dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1:1-dicarboxylate* (IV) in a manner which recalls the formation of diethyl hydriindenedicarboxylate (V) from *o*-xylylene dibromide (Perkin, T., 1888, 53, 7), and of diethyl pentamethylenedicarboxylate from  $\alpha\delta$ -dibromobutane (Haworth and Perkin, T., 1894, 65, 96; Staud, Ber., 1894, 27, 1229):



In the case of hexamethylene dibromide, Haworth and Perkin (*loc. cit.*, p. 599) found that only a very small proportion was converted into the *cycloheptane* derivative, the main product being the open-chain tetraethyl octanetetracarboxylate. In the present instance, however, the tendency to form the seven-membered ring is so great that even in the presence of two molecular proportions of ethyl malonate the reaction takes the same course as indicated above and one-half of the ethyl malonate is recovered unchanged.

Further, when diethyl 2:2'-ditolyl-*o,o'*-dicarboxylate is heated with sodium in benzene solution, it readily undergoes the Dieckmann condensation, and *ethyl 3:5-dibenzoo-1,3-cycloheptadione-1-one-carboxylate* (VI) is produced to the extent of 80 per cent. of the calculated amount:



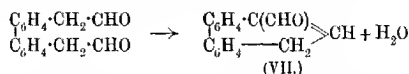
This compound gives an indigo-blue coloration with ferric chloride solution, and has pronounced acid properties, since its copper salt can be isolated by treatment with copper acetate without any precautions being taken to neutralise the acetic acid set free. This behaviour is in agreement with that of ethyl *cyclopentanonecarboxylate*, as contrasted with the corresponding *cyclohexanone* and *cycloheptanone* derivatives (Dieckmann, *Annalen*, 1901, **317**, 32), but the two cases are, of course, not strictly comparable, since the presence of an adjacent benzene nucleus would in any circumstances be expected to increase the acidity of the compound now described.

In the case of this reaction it is not possible to institute a comparison with the behaviour of the corresponding *o*-xylene derivative,\* because neither this, nor, indeed, any other compound not of purely aliphatic nature had hitherto been studied in this respect; but the yield obtained in the present case compares favourably with that obtained by Dieckmann (*loc. cit.*, p. 52) under similar conditions in the case of ethyl adipate (80 per cent.), whilst the yield of ethyl *cycloheptanonecarboxylate* obtained from ethyl suberate amounted only about 10 per cent. (Dieckmann, *loc. cit.*, p. 50).

\* It is intended to study the behaviour of diethyl *o*-phenylenediacetate in this respect.

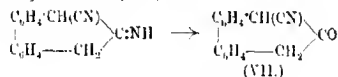


A further instance of the readiness with which ring-formation of the type under discussion takes place is contained in a recent paper by Weitzenböck\* (*Monatsh.*, 1913, **34**, 199), in which it is shown that *ωω'*-dialdehyde-2: 2'-ditolyl is condensed by sulphuric acid to an aldehydodibenzocycloheptatriene (VII):



The compounds now described, together with the dibenzocycloheptadienone previously obtained (Kenner and Turner, *loc. cit.*), render the more important derivatives of dibenzocycloheptadiene accessible by the usual methods, but the appearance of Weitzenböck's communication has necessitated the publication of the present paper before the experiments in this direction were as complete as it had been intended to make them. However, 1-amino-3: 5-dibenzocycloheptadiene (IX) has been prepared by reduction of cycloheptadienoneoxime with sodium, whilst 3: 5-dibenzo-Δ<sup>1:3:5</sup>-cyclo-

\* Weitzenböck refers (*loc. cit.*, p. 218) to a compound, m. p. 222°, obtained by heating aminocycloheptadiene with concentrated hydrochloric acid under pressure, and to which he is unable to assign a constitution. In conjunction with Miss E. G. Turner, I carried out a similar experiment under atmospheric pressure two years ago. It was, however, found that the product was a mixture of two compounds, one of which, m. p. 220° (over 90 per cent. of the whole) was insoluble in sodium carbonate solution, whilst the other, m. p. 219°, was soluble. The composition of each corresponded with that of the expected 2-cyano-2': dibenzo-Δ<sup>3:5</sup>-cycloheptadien-1-one (VIII).



*Non-acid portion:*

0.1122 gave 0.3400 CO<sub>2</sub> and 0.0944 H<sub>2</sub>O. C = 82.64; H = 4.89.

*Acid portion:*

0.1092 gave 0.3024 CO<sub>2</sub> and 0.0344 H<sub>2</sub>O. C = 82.3; H = 4.92.

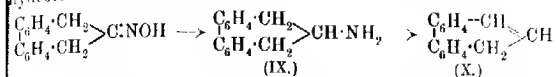
0.2063 „ 11.6 c.c. N<sub>2</sub> at 30° and 726 mm. N = 6.27.

C<sub>10</sub>H<sub>11</sub>ON requires C = 82.4; H = 4.72; N = 6.02 per cent.

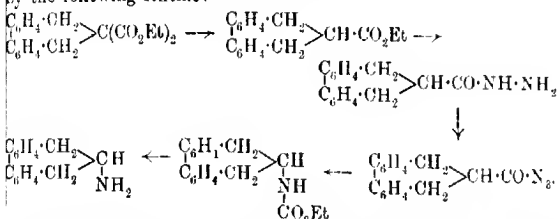
No depression of melting point was observed when the two compounds were mixed, and the two appeared to be interconvertible; further, the non-acid portion gave a brilliant wine-red coloration when heated with ferric chloride solution. The preliminary investigation thus seemed to show that the two compounds were desmotropically related, and the description of the experiments was deferred until the opportunity arose for a more thorough inquiry.

It may be pointed out that the numbering used by Weitzenböck in the designation of the above amino-compound is in contravention of the usual rules of the Geneva system, and as the compound in question has already been incorporated in this system (Kenner and Turner, *loc. cit.*) an alternative numbering can only lead to confusion and is therefore undesirable.

heptatriene (X) can be obtained by the dry distillation of the hydrochloride of the base:



This hydrocarbon is the analogue of indene, and, in view of the results obtained in the examination of the latter compound (Marckwald, *Ber.*, 1895, **28**, 1501; Thiele, *Ber.*, 1900, **33**, 3395; Annalen, 1906, **347**, 249), the further examination of dibenzocycloheptatriene is a matter of considerable interest. Unfortunately, the yields obtained by the above process are prohibitive, and attempts were therefore made to obtain dibenzocycloheptadienylamine in a more convenient manner. This object was attained by means of the series of reactions represented in outline by the following scheme:

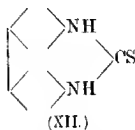


All these reactions give good yields, and it is hoped that, possibly by the use of the phosphate method of Harries (*Ber.*, 1901, **34**, 300) or the exhaustive methylation method of Willstätter (*Ber.*, 1907, **40**, 3979, and other papers), dibenzocycloheptatriene may be obtained in sufficient quantity to permit of its closer study. The distillation of barium 3:5-dibenzo-3:5-cycloheptadiene-1-monocarboxylate furnished a hydrocarbon, but this was apparently not dibenzocycloheptatriene, although Perkin and Révay (*T.*, 1894, **65**, 116) found that barium hydrindenecarboxylate is converted into indene under these conditions.

When the attempt is made to ascertain the cause of the readiness with which the formation of seven-membered rings from derivatives of 2:2'-ditolyl takes place, two modes of explanation suggest themselves.

The first assumes that the two benzene nuclei are not, as is usually considered and is required by the ordinary tetrahedral distribution of the valencies of the carbon atom, represented by XI), but are inclined to one another in such a manner as to ring the carbon atoms in the 2:2'-position as close to each other as in the ordinary ortho-position. This assumption makes

2: 2'-ditolyl directly comparable with *o*-xylene, as indeed has now been shown is the case, and has been advocated by Kaufler (*Annalen*, 1907, **351**, 152) to explain the production of some remarkable compounds of the type shown (XII):



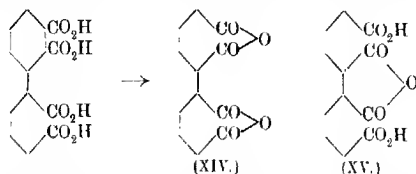
Kaufler assumes that the configuration of diphenyl is represented as shown (XIII), but does not specify whether he considers the two benzene nuclei to be in parallel planes or coplanar. In the former case ring-formation should be equally possible with 2: 2', 3: 3', and 4: 4'-derivatives of diphenyl, whilst the latter postulate, the equivalence of the 2: 2' and the 3: 3' positions. Quite apart from the severe strain either alternative would impose on the carbon atoms connecting the nuclei, both would appear to be disproved by the fact that diphenyl-3: 3'-dicarboxylic acid does not furnish an anhydride (Ullmann, *Annalen*, 1904, **332**, 73), whilst the 2: 2'-derivative (ordinary diphenic acid) is well known to do so. This argument, however, fails if the dicarboxylic acid be in reality a 3: 5'- as contrasted with a 3: 3'-derivative (compare Cui, Comfard, and Micklethwait, T., 1912, **101**, 2298), and it would be interesting to know whether 3: 3'-dinitrodiphenyl could be converted, for instance, into an azoxy-compound or a thiocarbamic derivative corresponding with XII. The author has not yet had the opportunity of studying other 3: 3'- or 4: 4'-derivatives in the respect.

The second explanation was brought forward in the previous communication, and, accepting the ordinary formula, was based on the view that the presence of double bonds in six- and seven-membered rings diminishes the strain and makes them more comparable with the saturated five-membered ring.\*

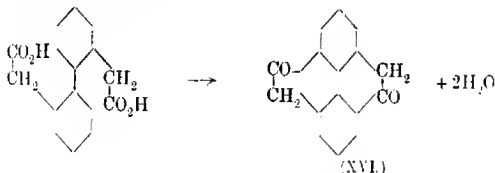
According to this explanation, the mean strain in the doubly unsaturated heptamethylene ring is 52°, and it would therefore be expected that a five-membered ring would be formed in preference to a seven-membered ring of this type. Experiments carried out

\* In this way, the mean strain in the benzene molecule was calculated as 2.6°; this calculation has since been carried out, apparently independently, by Boesche (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **14**, 1066; compare *Ann. Rep.*, 1911, p. 114) in connexion with some interesting speculations in regard to the benzene problem.

in this laboratory by Miss A. M. Mathews, B.Sc., are in agreement with this inference; 2:3:2':3'-diphenyltetracarboxylic acid is converted by acetyl chloride into the dianhydride (XIV), and no sign of the compound (XV) could be detected:



Since this hypothesis lays stress on the presence of the double bonds, it follows that the simultaneous formation of seven-membered rings in the 2:2' and the 6:6' positions of diphenyl should not be possible under the conditions used in the above experiments, and it will be necessary to carry out experiments in this direction. The synthesis of dihydroxypyrene\* (XVI), recently recorded by Weitzenböck (*loc. cit.*):

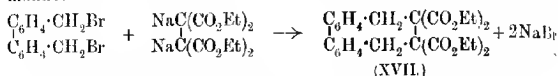


cannot be considered as evidence against this contention, since it is well known that six-membered rings are formed in the majority of cases almost as readily as five-membered rings. The reaction is of interest, however, as showing that the 2:2' and the 6:6' positions in diphenyl are relatively equivalent. This fact, on the hypothesis of inclined nuclei discussed above, can only be explained if the two benzene nuclei be in parallel planes. As this assumption is untenable (with the reservation already indicated), the theory that the nuclei are inclined must, in the author's opinion, be regarded with a very considerable measure of reserve, although it must be conceded that the production of Kautler's thiocarbamide derivatives does not admit of any other obvious explanation.

Experiments have also been made with the view of synthesising derivatives of dibenzoyl-octadiene. Thus, as *o*-xylene dibromide and disodium ethanetetracarboxylate condense with the formation of a tetrahydronaphthalene derivative (Perkin, T., 1888, 53, 7),

\* Experiments having for their object the synthesis of compounds of similar type have been in progress for some time in this laboratory.

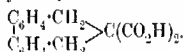
it was hoped that  $\omega\omega'$ -dibromo-2:2'-ditolyl might behave in a similar manner:



A product was actually isolated, the percentage composition of which agreed with this constitution (XVII), but the determination of its molecular weight by the cryoscopic method has thrown doubt on the accuracy of this formula, and the reaction must therefore be further investigated. It may be remarked that the mean strain in a *cyclooctadiene* ring amounts to  $8^\circ 49'$ , which is considerably less than that in the saturated *cycloheptane* ring.

#### EXPERIMENTAL.

##### 3:5-Dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1:1-dicarboxylic Acid,



A solution of diethyl malonate (8 grams) in freshly distilled anhydrous ether (120 c.c.) was added gradually to a hot solution of sodium (2.3 grams) in absolute alcohol (30 c.c.) in a reflux apparatus. Before the separation of diethyl sodiomalonate from the warm mixture had commenced, a solution of  $\omega\omega'$ -dibromo-2:2'-ditolyl (17 grams) in absolute ether (140 c.c.) was run in. The mixture at once became turbid, owing to the production of sodium bromide, and, after the initial vigorous reaction had subsided, the mixture was heated on the water-bath for three hours. After filtration, the ether was removed from the solution, which was neutral to litmus, by distillation. The residual oil consisted of almost pure diethyl dibenzocycloheptadienedicarboxylate, and slowly became converted into a mass of crystals. In order to isolate the dicarboxylic acid, the oil, dissolved in absolute alcohol (250 c.c.), was returned to the flask containing the sodium bromide, and the mixture was then heated on the water-bath with a solution of potassium hydroxide (10 grams) in water (10 c.c.) until hydrolysis was complete, the operation requiring about half an hour. Unduly prolonged treatment resulted in partial elimination of carbon dioxide, for the final product had a low melting point, but gave satisfactorily pure material when subsequently converted into the monocarboxylic acid. The product of hydrolysis was worked up in the usual manner, the dicarboxylic acid being precipitated from the solution of its potassium salt after the latter had been extracted with ether to remove impurities, which rendered the solution slightly turbid. The yield of crude product was nearly 90 per

cent. of that calculated. After crystallisation from dilute alcohol, the acid was obtained in colourless prisms, which melted at  $205^{\circ}$  with loss of carbon dioxide:

0.1106 gave 0.2922  $\text{CO}_2$  and 0.0514  $\text{H}_2\text{O}$ .  $\text{C}=72.05$ ;  $\text{H}=5.16$ .

$\text{C}_{17}\text{H}_{14}\text{O}_4$  requires  $\text{C}=72.34$ ;  $\text{H}=4.97$  per cent.

The *diethyl* ester, isolated in the manner already described, was purified by crystallisation from light petroleum (b. p.  $40-60^{\circ}$ ), and formed rhombic crystals, which melted at  $64^{\circ}$ :

0.1464 gave 0.3992  $\text{CO}_2$  and 0.0872  $\text{H}_2\text{O}$ .  $\text{C}=74.37$ ;  $\text{H}=6.62$ .

$\text{C}_{21}\text{H}_{20}\text{O}_4$  requires  $\text{C}=74.54$ ;  $\text{H}=6.51$  per cent.

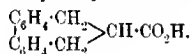
It was recovered unchanged after several days from its solution in alcohol, saturated with ammonia.

The *dihydrazide* was, however, produced when the diethyl ester was heated with hydrazine hydrate in alcoholic solution for several hours on the water-bath, and crystallised from alcohol in lustrous leaflets, which melted at  $246^{\circ}$ .

0.1556 gave 24.1 c.c.  $\text{N}_2$  at  $17^{\circ}$  and 748 mm.  $\text{N}=18.03$ .

$\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_4$  requires  $\text{N}=18.01$  per cent.

### 3:5-Dibenzo- $\Delta^{3:5}$ -cycloheptadiene-1-carboxylic Acid,



This acid was produced when the dicarboxylic acid just described was heated in an oil-bath at  $210^{\circ}$  until the evolution of carbon dioxide had ceased. The product was cooled and dissolved in sodium carbonate solution. After extraction with ether, the solution was acidified, and the precipitated acid obtained in good yield. The acid was purified by crystallisation from dilute alcohol, from which it separated in flat needles, melting at  $158^{\circ}$ :

0.1486 gave 0.4376  $\text{CO}_2$  and 0.0808  $\text{H}_2\text{O}$ .  $\text{C}=80.31$ ;  $\text{H}=6.04$ .

$\text{C}_{16}\text{H}_{14}\text{O}_2$  requires  $\text{C}=80.67$ ;  $\text{H}=5.88$  per cent.

The *barium* salt is best prepared by the gradual addition of an alcoholic solution of the acid to a hot solution of barium hydroxide, and separates from its solution in opaque clusters of needles, containing water of crystallisation, which is given up at  $180^{\circ}$ :

0.3144 gave 0.0392  $\text{H}_2\text{O}$  and 0.1052  $\text{BaSO}_4$ .  $\text{H}_2\text{O}=12.53$ ;

$\text{Ba}=19.40$ .

$(\text{C}_{16}\text{H}_{13}\text{O}_2)_2\text{Ba} \cdot 5\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=12.8$ ;  $\text{Ba}=19.67$  per cent.

When the anhydrous barium salt was heated under diminished pressure, it decomposed without any charring, and a colourless, viscous oil was produced which did not distil. The oil was isolated in the usual manner by extraction with ether, and in the course

of two months a few elongated hexagonal plates separated. These could not, however, be separated from the remainder of the material. No semicarbazone could be prepared from the product, which therefore did not contain a ketone. When, however, it was treated with alcoholic picric acid solution, a *picrate* was obtained, which crystallised in reddish-brown prisms, melting at 147–149°. The further examination of this compound was postponed until it could be compared with the *picrate* of dibenzocycloheptatriene, when it was found that a mixture of the two *picrates* melted at 110°. It therefore followed that the decomposition of the barium salt had not taken place in the same manner as that observed by Perkin and Révay in the case of hydrindeneacrylic acid, which was converted into indene (T., 1894, **65**, 246). The nature of this reaction will be the subject of closer investigation.

The *methyl* ester was prepared by saturating a cold solution of the acid in methyl alcohol with dry hydrogen chloride, and working up the mixture in the usual manner after three days. The ester was obtained as a highly refractive colourless liquid of high viscosity, boiling at 288°/181 mm., and gradually crystallised to radiate aggregates of plates, which melted at 44–45°:

0.2006 gave 0.5934 CO<sub>2</sub> and 0.1126 H<sub>2</sub>O. C = 80.68; H = 6.23.

C<sub>17</sub>H<sub>16</sub>O<sub>2</sub> requires C = 80.95; H = 6.35 per cent.

The *ethyl* ester resulted when the acid was esterified by means of sulphuric acid. It boiled at 244°/43 mm., and was a highly refractive viscous liquid, which did not solidify:

0.1746 gave 0.5184 CO<sub>2</sub> and 0.1058 H<sub>2</sub>O. C = 80.98; H = 6.73.

C<sub>18</sub>H<sub>18</sub>O<sub>2</sub> requires C = 81.20; H = 6.76 per cent.

The *chloride* was prepared in the usual manner by treating the acid with phosphorus pentachloride and boiled at 235°/60 mm.

0.3876 gave 0.2144 AgCl. Cl = 13.68.

C<sub>16</sub>H<sub>12</sub>OCl requires Cl = 13.84 per cent.

The *amide* was best prepared by the gradual addition of the chloride, previously heated to 100° to increase its mobility, to a cold aqueous ammonia solution (D 0.880) in a mortar. Each drop of the chloride was well triturated with the solution before any further addition was made, and the reaction was finally completed by warming the mixture on the water-bath. Owing to its high viscosity, the chloride is practically unattacked by ammoniac carbonate in the cold, and this method is therefore unsuitable for the preparation of the amide.

It also results when the methyl ester is heated under pressure with aqueous ammonia solution (D 0.880) at 130°, but the yield is only moderate.

By crystallisation from methyl alcohol, the amide was obtained in prisms, melting at 158°:

0.1626 gave 8.4 c.c.  $N_2$  at 18° and 728 mm.  $N=5.83$ .

$C_{16}H_{13}ON$  requires  $N=5.91$  per cent.

It did not dissolve in sodium hypochlorite solution, and the attempt to prepare the corresponding amine from it by the Hofmann method was therefore abandoned.

The *hydrazide* was prepared by heating the ethyl ester with excess of hydrazine hydrate in alcoholic solution on the water-bath until the mixture set to a solid mass when cooled. The hydrazide was separated by filtration from the liquor, and the latter usually furnished a further quantity of hydrazide after further heating. The compound was purified by crystallisation from alcohol, from which it separated in matted needles, melting at 176°. The hydrazide is only sparingly soluble in water, but readily so in old chloroform or hot alcohol:

0.1613 gave 16.4 c.c.  $N_2$  at 19.5° and 725 mm.  $N=11.37$ .

$C_{16}H_{16}ON_2$  requires  $N=11.11$  per cent.

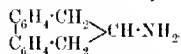
*Tetrabromo-3:5-dibenzon-Δ<sup>3:5</sup>-cycloheptadien-1-carboxylic Acid.*

A thin layer of finely ground dibenzocycloheptadienecarboxylic acid was exposed in a desiccator to the action of bromine vapour. After one week, the pasty product was transferred to a vacuum desiccator containing solid potassium hydroxide. It was then found that the acid had increased in weight by an amount which was about 5 per cent. more than that corresponding with the absorption of four atomic proportions of bromine. The tetrabromo-acid was sparingly soluble in alcohol, acetic acid, or the usual organic solvents, but dissolved easily in epichlorohydrin, and separated from this solvent in small clusters of opaque prisms, melting at 272°:

0.2366 gave 0.3217 AgBr. Br = 57.91.

$C_{16}H_{10}O_2Br_4$  requires Br = 57.77 per cent.

*1:1-Dimino-3:5-dibenzon-Δ<sup>3:5</sup>-cycloheptadiene.*



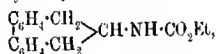
The preparation of this compound was effected in two ways, namely, from the hydrazide of dibenzocycloheptadienecarboxylic acid and from the oxime of dibenzocycloheptadienone.

(i) A solution of the hydrazide (5.5 grams) in hot absolute



alcohol (50 c.c.) was rapidly cooled, and treated at  $0^\circ$  with a solution of hydrogen chloride (1 gram) in absolute alcohol (10 c.c.). On shaking, the crystals of the hydrazide rapidly gave place to those of its hydrochloride, and the mixture became much more fluid. Amyl nitrite (3 grams) was then added, and after some time the mixture was allowed to regain the ordinary temperature, whereby almost everything passed into solution, with the exception of a few well-defined, transparent, colourless, rectangular prisms of the azide. After the yellow solution had been boiled until the evolution of nitrogen had ceased, the alcohol was removed by evaporation on the water-bath. The heating was continued for some time in order to remove the amyl esters as completely as possible, and the residual oil (5 grams) was then stirred with a little warm alcohol until crystallisation set in. The crystals were then pressed and further purified by solution in light petroleum (b. p.  $90-120^\circ$ ). Yield, 4 grams.

3:5-Dibenzo- $\Delta^{3:5}$ -cycloheptadienylurethane,



forms clusters of small prisms, melting at  $88^\circ$ :

0.2301 gave  $10.4$  c.c.  $\text{N}_2$  at  $16^\circ$  and  $736$  mm.  $N = 5.19$ .

$\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}$  requires  $N = 4.98$  per cent.

The urethane readily undergoes hydrolysis when it is heated with concentrated hydrochloric acid under pressure for six hours at  $150^\circ$ , dibenzocycloheptadienylamine hydrochloride being produced. If the crude oily urethane is hydrolysed without further purification, it is necessary to stir the dark-coloured oil formed in the reaction with ether, which extracts dibenzocycloheptadienecarboxylic acid. The presence of this acid is presumably due to the production of its ethyl ester in small amount (about 20 per cent.), when the azide is boiled with alcohol.

(ii) A boiling solution of dibenzocycloheptadienoneoxime (11 grams) in absolute alcohol (200 c.c.) was reduced by the gradual addition of sodium (20 grams) in the course of one hour. If necessary, the dissolution of the sodium was completed by the addition of a small quantity of absolute alcohol, and the mixture was then diluted and subjected to steam distillation. The distillate was acidified with hydrochloric acid and evaporated to dryness, whereby the hydrochloride of the base (5 grams) was left. The later portions of the distillate contained another product (possibly dibenzocycloheptadienone), which was readily separated from the hydrochloride by extracting the concentrated solution with ether.

Dibenzocycloheptadienylamine hydrochloride forms lustrous

needles, moderately soluble in dilute hydrochloric acid. It melts at  $287^{\circ}$ , and decomposes about  $300^{\circ}$ :

0.1928 gave 10.2 c.c.  $N_2$  at  $21^{\circ}$  and 731 mm.  $N=5.94$ .

$C_{15}H_{15}N \cdot HCl$  requires  $N=5.70$  per cent.

The *platinichloride* is a canary-yellow precipitate, which could not be obtained in a crystalline condition. It melts at  $268^{\circ}$ :

0.3576 gave 0.0838 Pt.  $Pt=23.38$ .

$(C_{15}H_{15}N)_2H_2PtCl_6$  requires  $Pt=23.53$  per cent.

An aqueous solution of the hydrochloride gave a white precipitate with ammonium oxalate, and a yellow one with potassium dichromate solution. No precipitate was produced with ferric chloride or with potassium iodide.

*Acetyldibenzocycloheptadienylamine* was prepared by heating the hydrochloride with acetic anhydride and sodium acetate at  $140^{\circ}$ . After crystallisation from dilute alcohol, it formed slender, silky needles, melting at  $147^{\circ}$ :

0.1668 gave 8.4 c.c.  $N_2$  at  $17^{\circ}$  and 739 mm.  $N=5.79$ .

$C_{17}H_{17}ON$  requires  $N=5.56$  per cent.

3:5-Dibenzo- $\Delta^{1:3:5}$  cycloheptatriene,  $\begin{matrix} C_6H_4-CH \\ C_6H_4-CH_2 \end{matrix} > CH$ .

Dibenzocycloheptadienylamine hydrochloride was heated in a drawn-out test-tube until decomposition was complete. Only a small amount of oil distilled over, and this was converted by treatment with a saturated alcoholic picric acid solution into a reddish-brown picrate. A larger quantity was obtained from the oil contained in the test-tube, after separation from the ammonium chloride also present, by extraction with ether and drying in the usual manner. The yield was only moderate.

*Dibenzocycloheptatriene picrate* crystallises from alcoholic solution in copper coloured needles, which melt at  $137^{\circ}$ :

0.1460 gave 0.3200  $CO_2$  and 0.0530  $H_2O$ .  $C=59.78$ ;  $H=4.03$ .

0.1524 „ 13.8 c.c. at  $12^{\circ}$  and 715 mm.  $N=10.2$ .

$C_{18}H_{12}C_6H_5O_3N_3$  requires  $C=59.86$ ;  $H=3.56$ ;  $N=9.93$  per cent.

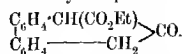
Diethyl 2:2'-Ditolyl- $\omega\omega'$ -dicarboxylate,  
 $CO_2Et \cdot CH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot CH_2 \cdot CO_2Et$ .

This compound was prepared by esterifying the dicarboxylic acid in the presence of sulphuric acid in the usual manner. After crystallisation from light petroleum (b. p.  $60-80^{\circ}$ ), it was obtained in large, rhombic crystals, which melted at  $49^{\circ}$ :

0.1774 gave 0.4778  $CO_2$  and 0.1060  $H_2O$ .  $C=73.45$ ;  $H=6.64$ .

$C_{20}H_{12}O_4$  requires  $C=73.65$ ;  $H=6.75$  per cent.

*Ethyl 3:5-Dibenzo- $\Delta^{3:5}$ -cycloheptadien-1-one-2-carboxylate,*



Sodium powder (2.1 grams), prepared in presence of toluene in the usual manner, was covered with dry benzene (150 c.c.) in a reflux apparatus, and diethyl 2:2'-ditolyl- $\omega\omega'$ -dicarboxylate (14.6 grams) was then added. The mixture was raised to the boiling point, and a vigorous reaction at once set in. After this had moderated, the heating was continued for about one hour, by which time all the sodium had disappeared, and the mixture began to bump violently, owing to the separation of sodium ethoxide. The reddish liquid was then decomposed by dilute sulphuric acid, the oily layer separated and washed, and the crude ester isolated by distilling off the benzene. By shaking the ethereal solution of the residual oil with aqueous copper acetate solution, the copper salt of the condensation product was precipitated, whilst any unchanged ester was retained by the ether. Yield, 11.2 grams.

The *copper* salt is a dirty light green powder, dark green in solution. It is readily soluble in chloroform, epichlorohydrin, or benzene, sparingly so in ether, and insoluble in acetone, alcohol, or water. It separates from a mixture of epichlorohydrin with alcohol in an indistinctly crystalline condition, and melts at 253°. By decomposition with nitric acid and careful ignition:

0.3701 gave 0.0463 CuO. Cu = 10.01.

(C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>)<sub>2</sub>Cu requires Cu = 10.23 per cent.

The free ester was obtained by shaking the solution of the copper salt in benzene with dilute sulphuric acid. Its alcoholic solution is coloured indigo blue by ferric chloride. When the attempt was made to distil it under diminished pressure (30 mm.) it decomposed, and nothing passed over. The residue in the flask no longer gave a coloration with ferric chloride.

*Condensation of  $\omega\omega'$ -Dibromo-2:2'-ditolyl with Tetraethyl Ethane-tetracarboxylate.*

Finely powdered dibromoditolyl (3.4 grams) and tetraethyl ethanetetracarboxylate (3.18 grams) were heated with a solution of sodium (0.45 gram) in absolute alcohol (10 c.c.) at 120–140° under pressure for five hours. The product, which was neutral to litmus, was freed from alcohol by evaporation. The residual oil was stirred with cold water, and quickly solidified. By crystallisation from light petroleum (b. p. 40–60°), rectangular blocks (1.2 grams) were obtained, which melted at 108.5°:

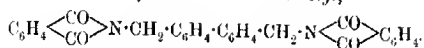
0.1256 gave 0.3120  $\text{CO}_2$  and 0.0758  $\text{H}_2\text{O}$ .  $\text{C}=67.74$ ;  $\text{H}=6.71$ .

0.1160 „ 0.2878  $\text{CO}_2$  „ 0.0662  $\text{H}_2\text{O}$ .  $\text{C}=67.67$ ;  $\text{H}=6.34$ .

$\text{C}_{28}\text{H}_{32}\text{O}_8$  requires  $\text{C}=67.76$ ;  $\text{H}=6.45$  per cent.

The composition of the product thus corresponds with that of the expected tetraethyl dibenzocyclooctadienetetracarboxylate, but determinations of the molecular weight by the cryoscopic method, in benzene solution, kindly carried out by Mr. W. A. Silvester (Found, 364, 387. Calc., 496), are not in agreement with this formula, and it will therefore be necessary to examine this compound more closely.

*ωω'-Diphthalimino-2:2'-ditolyl*,



This compound was readily obtained when dibromoditolyl was heated with two molecular proportions of potassium phthalimide at  $150^\circ$  for one hour. The solid mass was powdered, extracted with hot water, and the residual diphthalimino-derivative purified by crystallisation from glacial acetic acid. It forms prisms, which melt at  $256^\circ$ :

0.1962 gave 11.0 c.c.  $\text{N}_2$  at  $30^\circ$  and 716 mm.  $\text{N}=6.17$ .

$\text{C}_{30}\text{H}_{20}\text{O}_4\text{N}_2$  requires  $\text{N}=5.93$  per cent.

By hydrolysis with concentrated hydrochloric acid at  $180^\circ$ , *ωω'-diamino-2:2'-ditolyl dihydrochloride* is produced.

The reactions of the compounds described above are under investigation, and the general question of ring formation from ditolyl derivatives is being studied along the lines indicated in this paper.

In conclusion, the author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which covered part of the expenses of this investigation.

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LXX.—*The Vapour Pressures of the Lower Alcohols and their Azeotropic Mixtures with Water. Part I. Ethyl Alcohol.*

By RICHARD WILLIAM MERRIMAN, M.A.

AN azeotropic mixture is a mixture of liquids which distils at a constant temperature, when the pressure is kept constant, without change of composition. The study of such mixtures, since the pioneering work of Roscoe and Dittmar (T., 1859, **12**, 128), has been confined to a few workers, partly because of the tedious nature of the work, and partly because no explanation of the formation of such mixtures has been brought forward, so that the results obtained cannot be used in testing the validity of theoretical deductions.

The work has, however, led to many important technical applications, such as the preparation of strong acids (Roscoe and Dittmar, *loc. cit.*; Roscoe, T., 1860, **13**, 146; 1862, **15**, 270), the preparation of chloroform for medical use (Wade and Finchemore, T., 1904, **85**, 938), and the preparation of absolute alcohol (Young, T., 1902, **81**, 707). The recent paper by Forster and Withers (this vol., p. 266) on Vaubel's phenyl-di-imine has called the attention of organic chemists to the importance of always bearing in mind the possibility of the formation of such mixtures.

The azeotropic mixtures which the lower alcohols form with water at atmospheric pressure have been studied by various workers since the time of Erlenmeyer (*Annalen*, 1863, **126**, 307), and were completely worked out by Young and Fortey (T., 1902, **81**, 717).

The present work was commenced with the idea that the study of the binary azeotropic mixtures of a homologous series of alcohols and water, at different pressures, might produce data which would be of assistance in the formulation of a theoretical explanation of the existence of such mixtures.

The compositions of the azeotropic mixtures of ethyl alcohol and water, at various pressures, have already been determined (Wade and Merriman, T., 1911, **99**, 997). The results followed the rule, from which there are only one or two exceptions, that the percentage of the constituent of lower boiling point, in a mixture of minimum boiling point, increases as the pressure decreases. The work of Forster and Withers (*loc. cit.*) also supports the rule.

In the present communication, determinations of the vapour pressure of ethyl alcohol by the dynamic method are described, and the view is expressed that this method gives more trustworthy results than other methods. Determinations of the boiling points

of the azeotropic mixtures, made up according to the results previously obtained (Wade and Merriam, *loc. cit.*), are also given, and are compared with the boiling points of dry alcohol, at the same pressures.

### I.—*Preparation and Density of Absolute Alcohol.*

(a) Ten litres of 95 per cent. alcohol were boiled in a copper drum for twenty-four hours with 4 kilos. of quick-lime made from marble. On distilling the product, spirit containing about 0.5 per cent. of water was obtained. This formed the stock, which was carefully dried, as required, in batches of 700 grams.

(b) 700 Grams of the 99.5 per cent. alcohol were boiled on the water-bath, under a reflux condenser, with 150 grams of quick-lime made from marble, taking the usual precautions for preventing the absorption of atmospheric moisture. After six hours, the product was distilled from the water-bath, a double spray trap being fixed on to the flask. The first 50 grams were rejected; the distillate obtained by boiling almost to dryness (about 600 grams) had a density of  $0.80630$   $0^{\circ}/4^{\circ}$ , and thus contained 0.006 per cent. of water. By continuing the heating, more alcohol slowly distilled from the apparently dry line. In this way 25 grams were obtained; the density was  $0.80634$   $0^{\circ}/4^{\circ}$ , corresponding with 0.02 per cent. of water. When the main fraction was distilled, the contents of the flask were probably at a temperature of not more than  $80^{\circ}$ , but when the last few grams were slowly distilled from the solid residue, the temperature must have reached  $100^{\circ}$ . It follows that calcium hydroxide at  $100^{\circ}$ , in the presence of alcohol, is partly dehydrated. This observation was repeated several times. Therefore in the preparation of absolute alcohol, both the first and last fractions should be rejected.

(c) The alcohol of specific gravity  $0.80630$   $0^{\circ}/4^{\circ}$  was again treated with lime, and the density of the main fraction was  $0.80628$   $0^{\circ}/4^{\circ}$ . Another treatment with lime left the density unchanged.

(d) On treating this alcohol with metallic calcium, carefully washed with dry alcohol, the density still remained the same.

(e) 200 Grams of the alcohol of density  $0.80628$   $0^{\circ}/4^{\circ}$  were mixed with 3 grams of washed calcium and distilled through an eight-section Young evaporator column. No alteration in the density took place.

(f) Starting once more with 99.5 per cent. alcohol and using metallic calcium instead of lime, the final product with density  $0.80628$   $0^{\circ}/4^{\circ}$  was reached with much greater difficulty and loss of material. Many other dehydrating agents were tried, but lime was found to be by far the most efficient. In all, about forty

samples of absolute alcohol were prepared, with density 0.80628 0°/4°, and no subsequent treatment would reduce the density.

The densities were determined in the manner recently described (Wade and Merriman, T., 1912, **101**, 2429).

This density confirms the value 0.80627 0°/4° obtained by Young (T., 1902, **81**, 717), and 0.80628 0°/4° by Klason and Norlin (*Arkiv. Kem. Min. Geol.*, 1906, **8**, No. 24, 1). The final product contained only small traces of acetaldehyde (less than 1 in 5000), and as this small amount cannot affect the density or boiling point, it was not thought worth while to run the risk of introducing other impurities in an endeavour to remove it.

(g) Samples of alcohol were prepared from potassium ethyl sulphate by Klason and Norlin's method (*loc. cit.*). They had the same densities and boiling points as the previous samples.

## II.—The Vapour Pressure of Ethyl Alcohol.

The best method of determining vapour pressures is to distil large quantities of the pure liquid through a Young evaporator column, using efficient means for maintaining constant pressures (Wade and Merriman, T., 1911, **99**, 984). A distillation, at the rate of one drop per second, can be carried out when the boiling point is six or seven degrees above room temperature, without superheating the thermometer at the top of an eight section column. Therefore if a small room kept at  $-7^{\circ}$  were available, the boiling points could

TABLE I.  
*Experimental Boiling Points of Ethyl Alcohol.*

Pressure in mm.	Boiling point.	Pressure in mm.	Boiling point.
30.8	14.34°	448.8	65.55°
31.5	16.10	498.7	68.00
37.6	17.50	549.7	70.30
43.6	20.00	597.1	72.30
44.6	20.30	649.7	74.37
49.5	22.08	700.7	76.24
57.2	24.39	750.2	77.98
72.5	28.53	769.5	78.62
75.0	29.20	800.1	79.60
78.8	30.04	899.7	82.63
98.8	34.18	999.6	85.39
132.7	39.71	1021.5	86.01
150.8	42.23	1099.9	87.37
198.1	47.70	1199.6	90.30
218.1	49.68	1301.0	92.55
247.0	52.26	1401.7	94.62
350.3	56.46	1501.1	96.56
347.5	59.66	1599.9	98.39
490.5	62.89	1679.0	99.76

be determined from 0° upwards. The lowest temperature obtainable by the author was 7°, so that another method had to be used for temperatures below 14°. The Anschütz thermometers used in this work had been compared with standards, and the temperatures are reduced to the hydrogen scale in the latitude of Paris. At least, two different thermometers were used at each pressure.

For low pressures, the apparatus used in the case of ethyl acetate (Wade and Morrigan, T., 1912, 101, 2438) was modified by adding a second thermometer, the bulb of which was just above the surface of the liquid, and was wrapped in cotton wool which dipped in the liquid. The whole apparatus was loosely wrapped in cotton wool, and no external heat was used during the experiment. When the pressure was kept constant for some time, the two thermometers registered the same temperature, after being corrected for the change of zero due to the vacuum (Ramsay and Young, *Phil. Trans.*, 1884, 173, ii, 472).

Every care must be taken to keep the pressure constant, as the thermometer in the liquid is slower than the other in reaching a new constant temperature. The reason for choosing this method is that the same apparatus is used in the study of the azeotropic mixtures at low temperatures. A mixture of known composition is placed in the flask, and after half of it has boiled away, the composition of the residue is determined.

TABLE II.

*Experimental Boiling Points of Ethyl Alcohol at Low Pressures.*

Pressure in mm.	Boiling point.	Pressure in mm.	Boiling point.
10.1	-2.05°	20.8	8.11
11.3	-0.20	21.7	8.74
12.5	+0.53	22.3	9.07
12.8	0.87	23.0	9.60
13.3	1.30	25.0	11.05
13.9	2.15	26.6	11.93
15.0	2.90	27.3	12.30
15.9	3.99	28.1	12.93
16.8	4.94	29.7	13.68
17.3	5.34	30.5	14.01
18.1	6.25	31.1	14.35
19.4	7.11		

The first differences of the experimental results were plotted against the mean temperatures. This curve, which required only slight modification, was smoothed by means of the second difference curve. The experimental results were smoothed by its aid, and the results given in tables III, IV, and V were calculated.



TABLE III.  
*Vapour Pressures of Ethyl Alcohol from 0° to 25°.*

Temp.	Pressure in mm.	$dp/dt$ .	Temp.	Pressure in mm.	$dp/dt$ .
0°	12.0	0.90	13°	28.4	1.81
1	12.9	0.94	14	30.3	1.92
2	13.9	0.99	15	32.2	2.03
3	14.9	1.04	16	34.3	2.15
4	15.9	1.10	17	36.4	2.28
5	17.0	1.16	18	38.7	2.41
6	18.2	1.22	19	41.2	2.55
7	19.4	1.29	20	43.8	2.70
8	20.7	1.37	21	46.5	2.84
9	22.1	1.45	22	49.4	2.99
10	23.5	1.53	23	52.4	3.15
11	25.1	1.62	24	55.6	3.31
12	26.7	1.71	25	59.0	3.47

TABLE IV.  
*Vapour Pressures of Ethyl Alcohol from 0° to 105°.*

Temp.	Pressure in mm.	$dp/dt$ .	Temp.	Pressure in mm.	$dp/dt$ .
0°	12.0	0.90	55°	281.2	12.85
5	17.0	1.16	60	352.7	15.60
10	23.5	1.53	65	438.9	18.85
15	32.2	2.03	70	542.5	22.60
20	43.8	2.70	75	666.0	26.95
25	59.0	3.47	80	812.7	31.90
30	78.6	4.42	85	985.2	37.45
35	103.6	5.58	90	1187.0	43.70
40	134.9	6.95	95	1422.0	50.70
45	174.0	8.57	100	1694.0	58.40
50	222.2	10.50	105	2007.0	66.95

TABLE V.  
*Boiling Points of Ethyl Alcohol.*

Pressure in mm.	Boiling point.	$dt/dp$ .	Pressure in mm.	Boiling point.	$dt/dp$ .
50	22.20°	0.3312	760	78.30	0.0332
100	34.35	0.1846	800	79.61	0.0318
150	42.06	0.1316	900	82.65	0.0248
200	47.83	0.1033	1000	85.12	0.0244
250	52.47	0.0863	1100	87.96	0.0234
300	56.41	0.0738	1200	90.32	0.0226
350	59.84	0.0645	1300	92.52	0.0208
400	62.87	0.0576	1400	94.58	0.0200
450	65.59	0.0520	1500	96.53	0.0189
500	68.06	0.0471	1600	98.37	0.0179
550	70.33	0.0437	1700	100.12	0.0171
600	72.43	0.0406	1800	101.78	0.0163
650	74.39	0.0380	1900	103.37	0.0156
700	76.24	0.0356	2000	104.89	0.0150

The boiling point at 760 mm. is identical with Young's value (*loc. cit.*), and those at 400 mm., 1000 mm., and 1600 mm. with the values given by Schmidt (*Zeitsch. physikal. Chem.*, 1891, **8**, 620).

As the author wished to find the most trustworthy method for the determination of a large number of vapour pressures, he thought it worth while to examine some of the results obtained by means of Ramsay and Young's method (T., 1885, 47, 42).

Table VI gives a comparison of the present values with those of Ramsay and Young (*Phil. Trans.*, 1886, 177, i, 155) and of Richardson (T., 1886, 49, 762), which were all done in this way.

TABLE VI.

Temp.	(b.)	(c.)	(d.)	(e.)	(f.)	(g.)	(h.)
0°	12.0	12.24	12.24	—	—	12.24	12.24
5	17.0	17.15	—	18.17	19.57	17.15	17.25
10	23.5	23.50	23.77	24.81	26.22	23.5	23.75
15	32.2	32.10	—	33.84	33.40	32.1	32.40
20	43.8	43.95	44.00	45.6	45.76	43.8	43.95
25	59.0	59.50	—	61.03	61.27	59.5	59.15
30	78.6	78.05	78.06	78.72	82.21	80.2	78.80

Column (b) gives the present results; column (c) those of Ramsay and Young (*loc. cit.*), which have since been modified by Young (*Sci. Proc. Roy. Dubl. Soc.*, 1910, 12, 441), these modified values being given in column (d); columns (e) and (f) represent Richardson's values, calculated from his nearest experimental results.

The values of Ramsay and Young given in column (e) were found not to lie on a smooth curve, the value for 30° falling completely off the first difference curve. If most of the lower values are retained, that at 30° must be increased to 80.2 mm. in order to produce a smooth curve. These smoothed values are given in column (g). If, however, the modified values of Young are used, except that at 30°, the values given in column (h) are obtained on smoothing. These values agree in a remarkable way with the present values given in column (b), considering that each determination involves two readings of the manometer, besides those of the barometer and thermometer.

It seems, therefore, that Ramsay and Young's experimental results in the neighbourhood of 25° and 30° are somewhat inaccurate.

It will also be seen that Richardson's results given in columns (e) and (f) do not agree among themselves. The method seems to present great experimental difficulties. With the view of thoroughly testing whether Ramsay and Young's method was worth adopting as a standard, the author examined other results obtained with it. The values for acetic acid in Richardson's paper (*loc. cit.*), which purported to be fresh determinations made with a sample of the identical acid used by Ramsay and Young (T., 1885, 47, 43), were found to be merely reprinted from the latter paper. Although a test of the method by the results of different workers was not

available, Richardson himself did two series of experiments with the same sample of each liquid, in order to "check the results" (T., 1886, 49, 762).

Typical results are given in table VII.

TABLE VII.  
*Richardson's Experimental Results with the Ramsay and Young Method.*

Substance.	Temperature.	Pressures in mm.	
		1st Experiment.	2nd Experiment.
<i>iso</i> Butyl alcohol .....	66.0°	116.29	124.617
	78.7	226.82	229.45
	104.8	659.113	680.830
<i>iso</i> Amyl alcohol .....	95.65	193.08	190.41
<i>iso</i> Butyric acid .....	143.80	601.49	552.24
<i>iso</i> Valeric acid .....	133.0	175.159	174.01
	158.27	434.039	440.01

It will be seen that the work is not sufficiently accurate. The method was therefore not adopted, as it evidently requires prolonged practice, and as the static method is liable to give erratic results, the distillation method appears to offer the greatest chances of success, if a cold room is available for the lower temperatures.

The vapour pressures depend on the readings of three instruments. At low pressures the readings of the manometer and barometer are the most important, as a difference of 0.1 mm. means a difference of 0.1°. In this region pressures may be recorded to 0.05 mm., or in special cases to 0.01 mm. At atmospheric pressure a difference of 0.01° corresponds with a difference in pressure of 0.3 mm., and at two atmospheres with a difference of 0.6 mm. It is therefore clear that values recorded to 0.01 mm. or 0.001 mm. are meaningless. The experimental values, which should be numerous, should be smoothed by the method of first and second differences, and not by means of an empirical formula. No empirical formula \* hitherto tried gives results exact enough for smoothing purposes.

### III.—*Boiling Points of the Azeotropic Mixtures of Ethyl Alcohol and Water.*

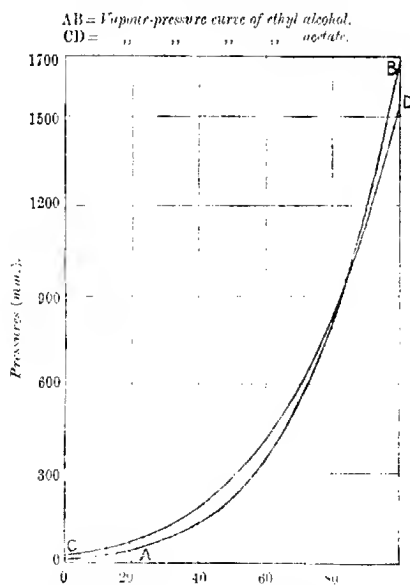
The mixtures were made up according to the values previously obtained (Wade and Merriman, T., 1911, 99, 1002). The results are given in table VIII.

\* Biot's formula, or the Ramsay and Young expression:  $R = R' + a(t - t')$ , gives only approximate results. The latter is obviously inapplicable to substances such as ethyl acetate and ethyl alcohol, the vapour pressure curves of which cut each other. Water is usually chosen as the standard substance, yet its vapour pressure curve is abnormal. Even for normal substances, the calculated values frequently differ from the observed values by many times the possible experimental error.

TABLE VIII.

Pressure in mm.	Per cent. of water in the azeotropic mixture.	Boiling point of azeotropic mixture.	Boiling point of ethyl alcohol.	$\Delta$ .	Boiling point of water.	$\Delta$ '.
1451.3	4.75	95.35°	95.58°	0.23°	119.14'	23.56
1075.4	4.65	87.12	87.34	0.22	110.09	22.66
760.0	4.4	78.15	78.30	0.15	100.00	21.70
401.6	3.75	63.04	63.13	0.09	83.27	20.14
198.4	2.7	47.63	47.66	0.03	66.31	18.65
129.7	1.3	39.20	39.24	0.04	57.06	17.82
94.9	0.5	33.35	33.38	0.03	50.62	17.24
70.0	0.0	—	27.96	0.00	44.63	16.67

The column under  $\Delta$  represents the differences between the boiling points of alcohol and of the azeotropic mixture; that under  $\Delta'$  gives the differences between the boiling points of alcohol and water.



The curve, drawn by plotting  $\Delta$  against the pressure, is as smooth as can be expected for such small differences of temperature.

The boiling points of the pure alcohol and of the azeotropic

mixture, at atmospheric pressure, are identical with the values obtained by Young and Forley (T., 1903, **81**, 768).

An interesting point should be noticed. At 1450 mm., when the difference between the boiling points of water and alcohol is  $23.56^{\circ}$ , a distillate containing 4.75 per cent. of water is obtained on distilling a mixture of alcohol and water, but at 70 mm., when the difference between the boiling points is only  $16.67^{\circ}$ , anhydrous alcohol distils over.

Any theory of azeotropic mixtures must explain this fact, that, as the boiling points of the pure liquids approach each other, separation by fractional distillation becomes easier.

A very curious point arises in the case of ethyl acetate and ethyl alcohol. The vapour-pressure curves of these liquids cross each other at a pressure of 948.1 mm. At this pressure each liquid boils at  $84.01^{\circ}$ ; at higher pressures the boiling point of ethyl acetate is above that of ethyl alcohol; at lower pressures ethyl alcohol has the higher boiling point. These liquids form an azeotropic mixture of minimum boiling point at atmospheric pressure (Wade, T., 1905, **87**, 1656). The study of the azeotropic mixtures of these liquids at high and low pressures, which is now in progress, might lead to important results. The diagram represents the vapour-pressure curves of ethyl acetate (Wade and Merriman, T., 1912, **101**, 2438) and of ethyl alcohol, showing the crossing at the above-mentioned point.

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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# LXXI.—*The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part III. Solubility of Carbon Dioxide at Pressures lower than Atmospheric.*

By ALEXANDER FINDLAY and THOMAS WILLIAMS, B.Sc. (1851 Exhibition Science Bursar, University College of Wales, Aberystwyth).

It has already been shown by Findlay and Creighton (T., 1910, **97**, 536) that the solubility of carbon dioxide in water is affected

very markedly by the presence of colloidal substances, the solubility in presence of the latter being in some cases greater, in some cases less, than in pure water. The form of solubility curve which was obtained in those cases was such that it became of interest to ascertain the values of the solubility at pressures lower than atmospheric; and we have therefore determined the solubility at 25° of carbon dioxide in water in presence of ferric hydroxide, dextrin, starch, gelatin, egg-albumen, silicic acid, suspensions of charcoal and of silica at pressures between 25° and 760 mm. of mercury, the results obtained being communicated in the present paper.

The apparatus employed was essentially the same as that used by Findlay and Creighton, but the manometer tube was now lowered so as to allow of pressures lower than atmospheric being measured. On account of the much smaller amount of gas absorbed at the low pressures, it was necessary to diminish the dead space as far as possible, so that the necessary correction might not constitute too large a fraction of the total gas volume measured. Even by reducing the dead space to 10 c.c., which was the lowest practicable value, the correction amounts, in some cases, to about 2 per cent. of the volume measured. We cannot therefore claim the same accuracy for our present determinations of the solubility as for those previously made, but the error may be taken as not exceeding 0.5 per cent.

In carrying out a determination of the solubility at low pressures, one proceeded as follows. The absorption pipette was filled with water or colloidal solution at 25°, whilst the tube communicating with the burette was filled with carbon dioxide under atmospheric pressure. A small filtering flask was attached to the lower tube of the absorption pipette, and a few c.c. of the liquid were forced into the flask by slightly increasing the pressure on the gas. Communication between the absorption pipette and the burette was then broken, the filtering flask was exhausted, and the requisite amount of liquid (about 35 c.c.) was withdrawn from the pipette. The pressure in the absorption pipette was now about one-fifth of an atmosphere. After the liquid in the pipette had acquired the temperature of the thermostat, the pressure in the burette was lowered to a suitable value, communication was opened between the burette and the pipette, and the solubility then determined as usual.

#### (a) *Water.*

The following values were obtained for the solubility in water of the carbon dioxide employed.

TABLE I.—*Solubility of Carbon Dioxide in Water.*

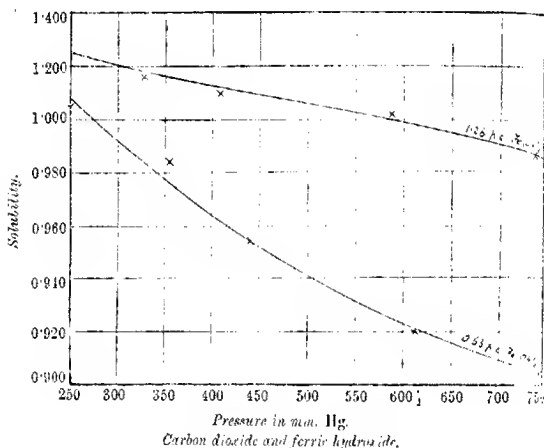
Pressure .....	271	392	495	667	768
Solubility .....	0.816	0.811	0.816	0.817	0.817
Pressure .....	263	382	479	651	752
Solubility .....	0.817	0.814	0.816	0.816	0.818

As the mean value of the solubility therefore, we find 0.816.

(b) *Ferric Hydroxide Solution.*

The ferric hydroxide solution was prepared as described by A. A. Noyes (*J. Amer. Chem. Soc.*, 1905, **37**, 94). It was freed from air by boiling under diminished pressure. The values of the solubility are given in table II (compare Fig. 1).

FIG. 1.

TABLE II.—*Solubility of Carbon Dioxide in Ferric Hydroxide Solutions.*

Concentration: 0.63 gram of  $\text{Fe}(\text{OH})_3$  in 100 c.c. of solution.

Density = 1.003.

Pressure .....	259	356	441	614	746
Solubility .....	1.041	0.984	0.951	0.920	0.901

Concentration: 1.26 gram of  $\text{Fe}(\text{OH})_3$  in 100 c.c. of solution.

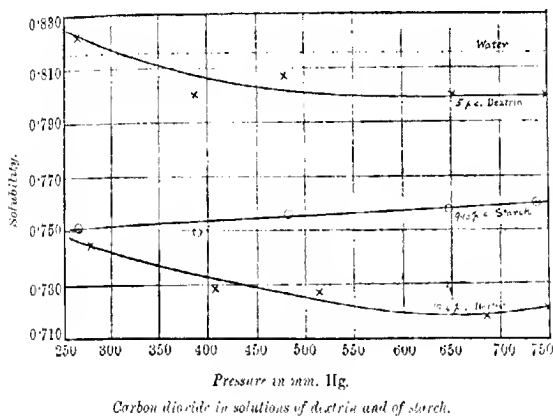
Density = 1.006.

Pressure .....	233	328	409	587	740
Solubility .....	1.286	1.165	1.107	1.023	0.989

(c) *Dextrin*.

The dextrin employed was the purest supplied by Kahlbaum. It contained a slight amount of impurity insoluble in water. This was separated from the solutions before the latter were employed, for absorbing carbon dioxide. The solutions were then rendered air-free by boiling under diminished pressure. The solubility values are given in table III (compare Fig. 2).

FIG. 2.

TABLE III.—*Solubility of Carbon Dioxide in Dextrin Solutions.*

Concentration: 5.00 grams of dextrin in 100 c.c. of water.

Density = 1.018.

Pressure .....	263	385	477	646	747
Solubility .....	0.820	0.802	0.809	0.800	0.799
Pressure .....	267	389	480	656	759
Solubility .....	0.823	0.798	0.804	0.799	0.799

Concentration: 19.4 grams of dextrin in 100 c.c. of solution.

Density = 1.065.

Pressure .....	271	399	501	679	760
Solubility .....	0.742	0.728	0.726	0.720	0.722
Pressure .....	283	414	527	688	755
Solubility .....	0.746	0.739	0.727	0.715	0.720



*(d) Starch.*

For these experiments Kahlbaum's pure soluble starch was employed. The solutions were again rendered air-free by boiling under reduced pressure.

TABLE IV.—*Solubility of Carbon Dioxide in Solutions of Starch.*  
(See also Fig. 2.)

Concentration: 4.6 grams of starch in 100 c.c. of solution.

Density=1.018.

Pressure .....	260	378	473	639	735
Solubility .....	0.787	0.784	0.786	0.789	0.789

Concentration: 5.1 grams of starch in 100 c.c. of solution.

Density=1.021.

Pressure .....	265	385	483	641	738
Solubility .....	0.783	0.785	0.783	0.783	0.783
Pressure .....	268	385	483	650	751
Solubility .....	0.788	0.786	0.787	0.784	0.784

Concentration: 9.13 grams of starch in 100 c.c. of solution.

Density=1.035.

Pressure .....	282	382	478	641	731
Solubility .....	0.751	0.752	0.757	0.758	0.760
Pressure .....	268	391	489	653	743
Solubility .....	0.751	0.746	0.755	0.758	0.760

We were able to confirm the observation made by Findlay and Creighton that the time required to saturate starch solutions is comparatively great. Moreover, the more concentrated the starch solution, the greater was the time required to saturate it with carbon dioxide.

*(e) Gelatin.*

French sheet gelatin was employed, the solutions being rendered air-free by boiling under diminished pressure. In the case of gelatin solutions, also, we were able to confirm the observation of Findlay and Creighton that saturation with carbon dioxide takes place comparatively slowly.

TABLE V.—*Solubility of Carbon Dioxide in Solutions of Gelatin.*  
(See also Fig. 3.)

Concentration: 2.6 grams of gelatin in 100 c.c. of solution.

Density = 1.006.

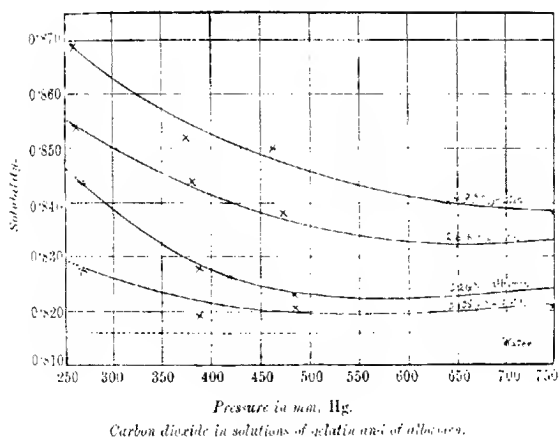
Pressure .....	264	383	471	651	762
Solubility .....	0.855	0.845	0.837	0.831	0.833
Pressure .....	262	380	477	649	756
Solubility .....	0.856	0.847	0.842	0.832	0.835
Pressure .....	264	380	470	651	759
Solubility .....	0.850	0.840	0.836	0.832	0.833

Concentration: 4.9 grams of gelatin in 100 c.c. of solution.

Density = 1.012.

Pressure .....	258	373	459	635	743
Solubility .....	0.870	0.847	0.847	0.839	0.838
Pressure .....	263	377	468	644	751
Solubility .....	0.868	0.854	0.852	0.841	0.838
Pressure .....	260	375	466	641	749
Solubility .....	0.870	0.854	0.850	0.841	0.839

FIG. 3.

(f) *Egg-Albumen.*

For these experiments Schuchardt's egg-albumen was used. This was dissolved in water filtered from an insoluble portion, and the albumen then precipitated by addition of ammonium sulphate to

the filtrate (see Hofmeister, *J. Physiol.*, 1898, **23**, 130). The precipitate so obtained was dissolved in water and dialysed until free from sulphate, a little toluene being added to prevent putrefaction.

The albumen obtained in this way, however, did not behave like that employed by Findlay and Creighton, which was prepared from fresh eggs. Thus it was found impossible to work with solutions of greater concentration than 0.2 per cent., on account of the fact that coagulation occurred during the course of the solubility determination. We have not been able to ascertain the reason of the discrepant behaviour, and although we give the results obtained with this egg-albumen, we propose to regard them to some extent as provisional.

TABLE VI.—*Solubility of Carbon Dioxide in Solutions of Egg-albumen.*

(See also Fig. 3.)

Concentration: 0.105 gram of albumen in 100 c.c. of solution

Density = 0.992.

Pressure .....	268	389	484	659	766
Solubility .....	0.826	0.816	0.819	0.819	0.819
Pressure .....	269	389	485	661	767
Solubility .....	0.829	0.822	0.822	0.824	0.822

Concentration: 0.21 gram of albumen in 100 c.c. of solution.

Density = 0.995.

Pressure .....	269	387	483	664	772
Solubility .....	0.814	0.827	0.823	0.826	0.824
Pressure .....	268	388	484	663	769
Solubility .....	0.813	0.829	0.824	0.823	0.824

(g) *Silicic Acid.*

The solutions of silicic acid were prepared by adding excess of hydrochloric acid to solutions of sodium silicate, and dialysing the liquid. The concentration is expressed in terms of  $\text{SiO}_2$ .

TABLE VII.—*Solubility of Carbon Dioxide in Solutions of Silicic Acid.*

(See also Fig. 4.)

Concentration: 0.45 gram of  $\text{SiO}_2$  in 100 c.c. of solution.

Density = 0.996.

Pressure .....	267	481	657	762
Solubility .....	0.816	0.813	0.816	0.818

Concentration: 0.95 gram of  $\text{SiO}_2$  in 100 c.c. of solution.

Density—0.999.

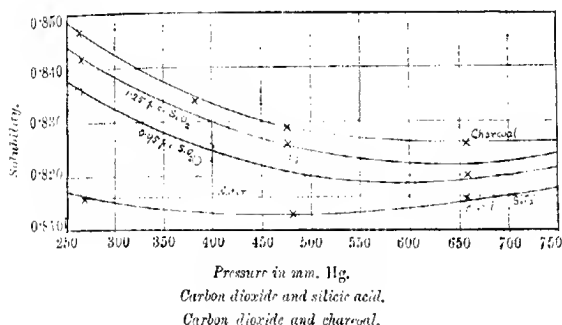
Pressure .....	262	385	481	652	756
Solubility .....	0.836	0.823	0.823	0.816	0.822

Concentration: 1.25 grams of  $\text{SiO}_2$  in 100 c.c. of solution.

Density—1.000.

Pressure .....	265	384	477	657	765
Solubility .....	0.842	0.826	0.826	0.820	0.824

FIG. 4.

*(h) Suspensions of Silica and of Charcoal.*

Suspensions of silica gave values for the solubility which did not appreciably differ from those in pure water; with a suspension of charcoal, the following values were obtained (see also Fig. 4):

Pressure .....	263	383	476	657	770
Solubility .....	0.847	0.834	0.829	0.826	0.826

*Discussion of Results.*

The results communicated in the preceding pages are found to be, on the whole, in harmony with those obtained at higher pressures by Findlay and Creighton. It is true that in the two series of determinations the actual values obtained for the solubility at atmospheric pressure are not in every case identical; but the discrepancies which are found are most probably to be accounted for by differences in the colloidal material employed. Such differences were marked in the case of solutions of egg-albumen, the

preparation which we employed behaving very differently from that used by Findlay and Creighton. This was evidenced more especially by the ready coagulation of the albumen employed in this investigation. There appears another difference in the albumen used by us as compared with that employed in the previous investigation, namely, that its presence led to an increase in the solubility of carbon dioxide. We have not been able to decide as to the reason for this, but we trust to be able to do so later. It may be remarked, however, that the curves of solubility which we have obtained with albumen agree with those most generally met with in the case of colloids.

If the values of solubility, however, are not in some cases identical with those previously obtained, we have found that the general trend of the curves is the same. This is seen very clearly in the case of the solubility curve for carbon dioxide in solutions of starch (Fig. 2), which appears to be a straight line indicating a gradually increasing solubility with increasing pressure—as was found also by Findlay and Creighton.

This curve deserves remark more especially because of the fact that it differs rather conspicuously from that found with other colloidal solutions. Previous investigation had shown that in the case of a number of colloids, the solubility curve exhibited a minimum point or else fell, with increasing pressure, to a constant value. By the extension of the investigation to lower pressures, the fact is established that this is the general behaviour. With the single exception of starch solutions, the solubility of carbon dioxide in colloidal solutions is exceptionally high at low pressures and diminishes with increase of pressure either to a minimum or to a constant value. Even in the case of dilute solutions of dextrin in which the solubility of carbon dioxide was found, at higher pressures, to be independent of the pressure, we now find that at lower pressures there is the same increase in the solubility of carbon dioxide as is met with in the case of most other colloids. By an investigation of the solubility of nitrous oxide which is being carried out in this laboratory, we hope to be able to decide whether this form of solubility curve is connected with the chemical nature of the gas, or depends only on the colloidal character of the solute. When that investigation is completed we hope to be in a better position to discuss the general form of the solubility curve. It is, however, apparent that the influence of colloids on the solubility of gases differs entirely from that of crystalloids. In the case of the latter, as was shown by Findlay and Shen (T., 1912, 101, 1459), the solubility is in harmony with Henry's law; but in the case of the former, this was no longer found. The present extension of the

investigation serves to confirm the unique and special behaviour of colloids with respect to gas solubility.

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## LXXII.—A New Iron Bacterium.

By ERNEST MOORE MUMFORD.

HAVING been recently occupied with a short study of *Clamydohormium*, the author visited the Bridgewater canal tunnels at Worsley, Lancashire, with the view of examining the growths found there, since the waters of the tunnels and basin are strongly charged with iron, due to the entrance of the colliery pump water.

The basin into which the tunnels debouch is connected to the Bridgewater canal by two short sections of canal, and these, together with the tunnels and basin, are practically disused by traffic. From the two tunnels there issues in one case fresh, clear water without iron, but from the other—the deeper of the two—a yellow, opaque liquid, which colours the whole basin a deep ochre.

The walls of the basin, the woodwork, the grass and trees dipping into the water are covered with a reddish-yellow growth, which at first sight appears to be an aggregation of *Crenothrix* or *Cladotrich*, but it was found that, although the growth and precipitated material were composed of ferric hydroxide, the most careful search failed to reveal more than one or two strands of higher bacteria. Since these were totally insufficient in numbers to account for the mass of ferric hydroxide, a careful bacteriological dilution and plating was carried out which resulted in the isolation of the organism causing the growth, which was found to be a hitherto unnamed bacillus.

Obtained from these sources, the pure culture of the bacillus was used to investigate the specific action of the organism.

For want of a suitable name, the organism will be designated in this paper under its laboratory number, "Bacillus M. 7."

### Description.

Growth on :	
Potato .....	Greenish-brown nodules, rising high in the middle, spreading very slowly.
Milk .....	Coagulation, liquid becomes straw-coloured, no acidity.
Gelatin-peptone bouillon .....	Liquefaction from surface and line of stab. Thick, white masses at the bottom of the liquid.
Peptone-bouillon .....	Opalescence, whitish strings appear.
Glucose in gelatin-peptone-bouillon .....	Shake culture—no gas.
Peptone water .....	No indole reaction.

Optimum temperature, 35–37°.

The organism is a facultative aerobe, and is of the average dimensions: 2.2 microns  $\times$  0.4 micron.

It is ciliated and exhibits a very varying motility; it occurs singly, and in short chains of three or four units.

The organism can form an endospore, but the majority of the bacilli under unfavourable conditions form a resistant involution form of varying shape, the general appearance of which is very similar to that presented by *Bacillus subtilis* under similar conditions.

An attenuated medium favours spore formation; a rich medium charged with the products of bacterial life favours involution forms.

#### *Action of the Organism on Iron Solutions.*

Since the organism is a truly facultative one, the study of its action falls naturally into two sections, namely, (i) under aerobic conditions, and (ii) under anaerobic conditions.

##### *(i) Under Aerobic Conditions.*

In both ferrous and ferric solutions it was found necessary to supply a trace of nitrogen. This was done by the addition of 0.005 per cent. of peptone, since the entire absence of nitrogen prevents the growth of the organism.

(a) *Ferrous solutions*.—A solution of ferrous ammonium sulphate (0.05 per cent.) was used. Complete precipitation of ferric hydroxide took place in twenty-four to thirty-six hours at 37°. The reaction is essentially aerobic, and proceeds to completion, no iron remaining in solution.

(b) *Ferric solutions*.—A solution of ferric ammonium citrate (0.05 per cent.) was used. Complete precipitation took place in twenty-four hours at 37°. In this case also the action was complete, no iron remaining in solution.

With regard to the necessity of nitrogenous material in the media, it is the opinion of the author that this is necessary, not primarily for the metabolism of the organism, but to provide, through the metabolic action, highly basic amino-compounds which unite with the highly ionised acids freed by the precipitation of the metallic bases by the action of the organism, since a small amount of precipitation takes place in the absence of nitrogen, but the action quickly ceases.

In support of this view may be mentioned the oxidation of phenol by *Bacillus helveticus*, which action can proceed without any nitrogenous material in the media, since the acid formed is ionised

only to a small degree. This is also in accordance with the effects of acid concentration in fermentations of cellulose.

(ii) *Under Anaerobic Conditions.*

The organism will not precipitate ferric hydroxide from either ferrous or ferric solutions in presence or absence of peptone. If, however, ferric hydroxide is originally present, it is changed into bog ore. This can be shown with ferric hydroxide precipitated either biologically or chemically. In this case, also, a minute trace of nitrogen is essential, but increasing quantities accelerate the speed of reaction.

This the author regards as being in accordance with the previous observations with regard to nitrogen in relation to aerobic precipitation, since in this case, when there is no acid product formed, the organism can produce the change to completion in the absence of nitrogen outside its own content, but if nitrogen is added, it is used solely in establishing the protoplasm of new organisms, and therefore increases the speed of reaction, but does not affect the completeness. The reaction takes about fourteen days at 37°.

The medium taken consisted of 500 c.c. of tap water, in which were suspended 5 grams of ferric hydroxide chemically prepared, and in which were dissolved 2.5 grams of peptone. This was inoculated, exhausted, and allowed to ferment at 37° for eighteen days. The flask then contained a clear, straw-coloured liquid and a black solid. No gas was evolved. The product was filtered and examined.

The residue, which was black, was dried and analysed. (Found,  $\text{FeO} = 9.00$ ;  $\text{Fe}_2\text{O}(\text{OH})_4 = 91.00$  per cent.) It consisted therefore of bog ore.

The filtrate was a yellow liquid, neutral towards litmus, but basic to acids, which on evaporation in a vacuum gave a yellowish-white solid having an unpleasant odour. On esterification, this solid yielded a mixture of the esters of amino-acids. If this filtrate is added to solutions containing iron (composed as before), precipitation takes place under certain conditions.

This naturally suggests that the organism produces an enzyme which is the cause of these reactions, and it was therefore necessary to determine if an enzyme could be separated and used to produce the effects associated above with the living organisms. It was found that if a solution in which the organism was growing freely was filtered through a Chamberland candle, the filtrate had the power of producing the reactions associated with that living organism.

This property is extended to the filtrate irrespective of the



presence of iron in the medium. It is produced only in minute quantities in the absence of nitrogen, but in order to secure the most reactive enzyme, the latter was produced by the action of the organism on peptone water.

*Isolation of the Enzyme.*

Peptone water, containing 10 grams per litre, is prepared and sterilised in the usual way. It is then inoculated, incubated at  $37^{\circ}$  for twenty-four hours, and filtered through a Chamberland candle. Thymol is added to the solution to prevent further bacteriological action.

The most reactive enzyme is obtained after twenty-four hours incubation. After a longer time it becomes weaker and disappears, being probably broken up by the bacteria as the pabulum becomes exhausted.

The enzyme is not destroyed by boiling or by evaporation in a vacuum, but is destroyed on being kept for forty-eight hours.

*Reactions of the Enzyme.*—The filtrate is not precipitated by picric acid, alcohol, ammonium sulphate (saturated solution), or sodium phosphotungstate (saturated solution), but is precipitated by Millon's reagent.

A white solid is obtained by evaporation in a vacuum. This white solid was, with the view of an approximate identification, esterified. On distillation and fractionation, several esters were separated, which were esters of the amino-acids usually associated with the partial, bacterial degradation of complex proteins. Some acids containing sulphur were also present.

*Experiments carried out with the Filtrate containing the Enzyme.*

Qualitative tests showed that the filtrate was able to produce the characteristic actions of the organism.

Solutions of ferrous salts are oxidised and precipitated; solutions of ferric salts are precipitated.

Analysis of the precipitate showed it to consist of ferric hydroxide in all cases. With the view of determining the optimum temperature of the enzyme, the simple precipitating reaction was studied.

Solutions of 10 c.c. of 0.05 per cent. of ferric ammonium citrate and 0.5 c.c. of the filtrate were used with the following results:

Precipitation at	Time.
$37^{\circ}$	1.5–2 hours
60	20–25 minutes
70	10–15 "
80	20–25 "

On boiling, partial precipitation took place in five to six minutes. If 1, 5, or 10 c.c. of the enzyme are taken, the speed is not increased.

The optimum temperature of the enzyme thus appears to be 70°.

Experiment has also shown that when the ratio between the filtrate and the iron solution varies between one part of filtrate and one part of iron solution, and one part of filtrate and fifty parts of iron solution, the speed or completeness of the precipitation is not appreciably affected. The precipitate in all cases is ferric hydroxide.

*Character of Enzyme.*—The filtrate was examined in the above manner after having been treated thus: (i) Fresh filtrate; (ii) filtrate kept overnight; (iii) filtrate boiled; and (iv) filtrate evaporated to dryness and extracted with water.

i.	Reactions as above .....	Active
ii.	No precipitation .....	Inactive
iii.	Reaction as (i), but slower .....	Active
iv.	Reaction as (i), but very slow .....	Active

The boiled solution only decomposes and becomes inactive in the course of several days.

#### *Basicity.*

*Active.*—50 c.c. fresh filtrate required 1.2 c.c. *N* 10-acid.

*Inactive.*—50 c.c. (kept overnight) required 7.5 c.c. *N* 10-acid.

*Active.*—50 c.c. boiled liquid required 12.8 c.c. *N* 10-acid.

There is therefore no apparent relation between basicity and enzymatic power. The fresh solution is more active than the boiled solution, although the latter precipitates at 70° in twenty to twenty-five minutes.

With regard to the mechanism of precipitation, the chief points may be summarised as follows:

The precipitation is produced by a crystalloid product formed by the organism from nitrogenous matter.

The optimum temperature of this crystalloid product, known as the "enzyme," is 70°.

It has not been found possible to produce the enzyme in appreciable quantity from media containing no nitrogen.

Starch and dextrose solutions in the presence of salts do not yield the enzyme in any appreciable quantity.

Therefore the organism, although living and reproducing in certain media, cannot produce the precipitating product except under certain conditions.

Since this is so this substance will depend for its nomenclature on the definition of an enzyme. Two broad conceptions of an enzyme are possible, namely, a product of the normal metabolism of the organism, and a product of the metabolism of the organism

dependent for its formation on the nature of the surrounding medium.

This enzymatic substance falls under the second definition, but not under the first, so that this precipitating agent must be described, according to the definition accepted, in the one case as a chemical precipitant produced by the organism under certain conditions, in the other case as a true enzyme.

#### *Summary.*

The bacillus is a true facultative organism, preferably an aerobe, and exercises a specific action on iron solutions.

The action of the bacillus on iron solution appears to proceed in two stages, in which the aerobic and anaerobic actions appear to be symbiotic, at any rate in nature.

The aerobic action is to precipitate ferric hydroxide from iron solutions, whilst the anaerobic action is to transform the ferric hydroxide thus precipitated to bog ore with partial reduction of the iron to a ferrous state.

To this organism are probably due the deposits of bog ore hitherto associated with the higher bacteria, since the latter have not the facultative power necessary to dehydrate and reduce the ferric hydroxide to bog ore.

I am indebted to Dr. G. J. Fowler for valuable suggestions and criticisms in the course of the above research.

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### LXXIII.—*Gossypetin.*

By ARTHUR GEORGE PERKIN.

GOSSYPETIN, a colouring matter of Indian cotton flowers, *Gossypium herbaceum* (T., 1899, **75**, 326), also present in the Egyptian variety (*ibid.*, 1909, **95**, 2181), and in the flowers of the *Hibiscus sabdariffa* (*ibid.*, 1909, **95**, 1855), has hitherto only been subjected to cursory examination. Originally considered to possess the formula  $C_{16}H_{12}O_8$ , it was subsequently shown that this is more probably  $C_{15}H_{10}O_8$ , the earlier preparation having apparently contained a trace of quercetin, which in appearance and many of its properties it closely resembles. Gossypetin forms oxonium salts

with mineral acids, its general reactions indeed possessing a flavonol character, and that it might reasonably be expected to possess such a constitution receives further support from its formula and the fact that it contains six hydroxyl groups. With the object of obtaining some more definite clue to its constitution, application was made to India for a large supply of the flowers, and my thanks are due to Mr. T. H. Burkill, Reporter on Economic Products to the Government of India, and to Mr. D. H. Hooper, the Officiating Reporter, for their liberal response to this request. The author again is indebted to Mr. H. M. Leake, Economic Botanist to the Government of the United Provinces of Agra and Oudh, for a similar favour, and also for certain special varieties of the flower which he himself had more recently investigated (*Proc. Roy. Soc.*, 1911, *B*, **83**, 447). For the preparation of the colouring matter a small quantity of the material was extracted in the laboratory, but an alcoholic extract and in part an aqueous extract of the main bulk were very kindly prepared by Messrs. Hirst, Brooke, and Hirst, of Leeds.

#### EXPERIMENTAL.

The alcoholic extract in quantities of 500 grams was added to 6 litres of hot water and boiled with 240 c.c. of hydrochloric acid (33 per cent.) for three hours. The tarry matter which had then separated was removed by filtration, and the yellow, semicrystalline product which was deposited from the clear liquid on cooling was collected and roughly purified by crystallisation from dilute alcohol. The yield was 32 grams. When operating with the aqueous extract of the flowers the process was of a more tedious nature, for this, when digested with boiling dilute acid, gave a voluminous, reddish-brown precipitate, consisting of a mixture of the colouring matter with much phlobaphen, and it thus appeared certain that these flowers contain as mineral salt a phlobatannin, readily soluble in water, although insoluble in alcohol. The product was collected, dried, and extracted with boiling alcohol, which dissolved the colouring matter and but little of the phlobaphen, the solution evaporated to a small bulk, cautiously diluted with boiling water, and the brownish-yellow deposit again crystallised from dilute alcohol.

When isolated by either of these methods the crude substance, in addition to non-tinctorial impurity, contained at least two colouring matters, which could be separated by the fractional crystallisation of their mixed acetyl derivatives. Thirty grams of substance, 120 c.c. of acetic anhydride, and fifty drops of pyridine were boiled for one hour, and after keeping overnight the crystals which had

separated were collected (the filtrate *A* being reserved for examination), and weighed 26 grams. On heating, this product sintered slightly at 190–196°, more markedly at 210°, and was completely melted at 226–228°. A further digestion for half an hour with 50 c.c. of boiling acetic anhydride was now resorted to, and the substance finally crystallised a third time from the same solvent. The crystals now weighed approximately 16 grams, and melted fairly sharply at 228–230°. In certain instances the last treatment with the anhydride was dispensed with, and the acetyl compound crystallised from a mixture of solvent naphtha and nitrobenzene. Finally, it was hydrolysed with sulphuric acid in the presence of acetic acid in the ordinary manner.

Found:  $C_{15}H_{10}O_8 = 55.59$ .

$C_{15}H_4O_8(Ac)_6$  requires  $C_{15}H_{10}O_8 = 55.76$  per cent.

An analysis of the gossypetin dried at 160° gave the following result.

Found: C = 56.70; H = 3.28.

$C_{15}H_{10}O_8$  requires C = 56.60; H = 3.14 per cent.

From the acetic anhydride mother liquors by evaporation and subsequent dilution with alcohol acetylated products of indefinite melting point were isolated, which, when fractionated, gave a further amount of acetyl-gossypetin. By these methods approximately 80 grams of pure gossypetin were obtained for experiment.

It has been shown (T., 1909, 95, 2181) that the Egyptian cotton flowers yield in addition to gossypetin a considerable amount of quercetin, and it was to be anticipated that the Indian variety would give a similar result. This proved to be the case, for an examination of the acetic anhydride mother liquor (*d*) revealed the presence of acetylquercetin, and, indeed, on long keeping it was frequently deposited in an almost pure condition, and could be obtained pure by crystallisation from a mixture of alcohol and acetic acid. It melted at 193–195°, and on hydrolysis gave quercetin, which was recognised by its well known properties. (Found, C = 58.62; H = 3.84.  $C_{21}H_{22}O_{12}$  requires C = 58.59; H = 3.90 per cent.)

Owing to the persistent sintering which occurs when the partly purified acetyl-gossypetin was heated to about 210°, a search for the isomeric acetylquercetagenin (T., 1913, 103, 212), which melts at 210–211°, was carried out, but without result. It is, however, considered still possible that in addition to quercetin and gossypetin a small amount of a third colouring matter is yielded by these flowers.

When fused with alkali gossypetin gives protocatechuic acid

(*lit.*), and this can be produced in abundance by dissolving the colouring matter in cold 50 per cent. aqueous potassium hydroxide, and allowing the solution to remain exposed to air for twenty-four hours with occasional shaking. It has not yet, however, been found possible to determine the character of the second nucleus present in this colouring matter by these methods.

*Methylation.*—Gossypetin (8 grams) in 90 c.c. of methyl alcohol was treated with 50 c.c. of methyl iodide, and to the boiling mixture a solution of 20 grams of potassium hydroxide in methyl alcohol was slowly added during two days. At the end of the first day it was necessary that when kept overnight air should be excluded so far as possible from the product, otherwise a considerable oxidation took place, with the formation of a blue-coloured potassium salt. The mixture, after being evaporated to a small bulk, was poured into ether (A) and on adding water a fine, almost colourless, crystalline precipitate separated in the aqueous layer. This was collected (3.8 grams), and when recrystallised from alcohol possessed a pale yellow appearance, but by the use of alcohol containing a little alcoholic potassium hydroxide was readily obtained in a colourless condition.

Found: C=62.44; H=5.52;  $\text{CH}_3=22.33$ .

$\text{C}_{13}\text{H}_{22}\text{O}_6$  requires C=62.68; H=5.47;  $\text{CH}_3=22.38$  per cent.

*Gossypetin hexamethyl ether*,  $\text{C}_{13}\text{H}_{14}\text{O}_2(\text{OMe})_6$ , separates as a rule in colourless needles, although occasionally in the prismatic form, and on one occasion the needles which had separated on long keeping in contact with the alcohol gradually changed into the latter modification. It is sparingly soluble in cold alcohol, and melts at  $170-172^\circ$ .

The ethereal liquid (A) on evaporation yielded a small amount of crystalline substance; this separated from alcohol in yellow needles, but insufficient for satisfactory examination.

In order to study the products of the hydrolysis of the hexamethyl ether, to a solution of 2.8 grams of potassium hydroxide in 14 c.c. of 80 per cent. alcohol 1.4 grams of the substance were added, and the mixture boiled for six hours. After removal of the alcohol the residue was dissolved in a little water, and treated with carbon dioxide, which caused the separation of a colourless, crystalline precipitate. This was collected, a further amount being isolated from the aqueous liquid by means of ether. It was purified by recrystallisation from alcohol.

Found: C=56.02; H=6.08;  $\text{CH}_3=23.55$ .

$\text{C}_{11}\text{H}_{18}\text{O}_6$  requires C=56.24; H=6.25;  $\text{CH}_3=23.43$  per cent.

*Gossypitol tetramethyl ether*, the name proposed for this sub-

stance, forms long, colourless needles, melting at  $115-116^{\circ}$ , and sparingly soluble in cold alcohol.

The bicarbonate solution when neutralised with acid gave a colourless precipitate, which, on crystallisation from dilute alcohol, separated in needles melting at  $180-182^{\circ}$ , and consisted of veratric acid.

*Ethylation.*—The yield of substance obtained by methylating gossypetin being somewhat poor, the ethylation of the colouring matter was now studied. Ten grams of gossypetin in 120 c.c. of absolute alcohol and 60 grams of ethyl iodide were boiled with addition of 25 grams of potassium hydroxide in alcohol a little at a time during two days, care being taken as in the methylation process to avoid admission of air. At the end of the operation the mixture was filtered, the filtrate evaporated to a small bulk, and poured into much ether whilst hot, as otherwise it gelatinises. The solution, which yielded practically nothing to dilute alkali, on evaporation gradually deposited needles, which were collected (6.35 grams) and washed with a little ether. By crystallisation from very dilute alcoholic potassium hydroxide a trace of a yellow compound was removed.

Found: C=66.37; H=7.20; Et=35.85.

$C_{27}H_{34}O_8$  requires C=66.66; H=7.00; Et=35.80 per cent.

*Gossypetin hexaethyl ether*,  $C_{15}H_{14}O_2(OEt)_6$ , is colourless, sparingly soluble in cold alcohol, and melts at  $144-146^{\circ}$ .

The hydrolysis of this compound (7.1 grams) was carried out as with the methyl derivative, employing the same proportions of alcohol and alkali. The product after being evaporated to dryness was dissolved in water, and treated with carbon dioxide, yielding 3.84 grams of a crystalline precipitate, whereas 0.2 gram of the same product was isolated from the aqueous liquid by means of ether. It was purified by crystallisation from alcohol.

Found: C=61.46; H=7.72; Et=36.25.

$C_{16}H_{24}O_6$  requires C=61.53; H=7.69; Et=37.17 per cent.

*Gossypitol tetraethyl ether* consists of colourless needles melting at  $110-111^{\circ}$ , sparingly soluble in cold alcohol. The mother liquors obtained during the purification of this compound contained a small amount of a more soluble substance, which remained after evaporation as a viscid mass.

The bicarbonate solution when neutralised with acid gave a crystalline precipitate, which was collected (2.392 grams) and recrystallised from dilute alcohol. (Found. C=62.83; H=6.76.  $C_{11}H_{14}O_4$  requires C=62.8; H=6.66 per cent.)

*J*<sub>1</sub> was obtained in long, colourless needles melting at 166–167°, and evidently consisted of protocatechuic acid diethyl ether.

As was anticipated, gossypitol tetraethyl ether proved to contain a carbonyl group, and an oxime could be readily prepared from it by Lapworth and Steele's method (T., 1911, 99, 1884). Half a gram of the ketone, 0.5 gram of anhydrous sodium acetate, 0.2 gram of hydroxylamine hydrochloride, and 25 c.c. of alcohol were boiled for five hours, the main bulk of the alcohol then distilled off, and the residue treated with hot water. The crystals which separated were collected, washed with hot carbon disulphide, and recrystallised from benzene, from which they separated in long, colourless needles, melting at 127–129°.

Found: C=58.59; H=7.77; N=4.31; Et=34.95.

$C_{16}H_{22}O_6N$  requires C=58.65; H=7.64; N=4.28;

Et=35.17 per cent.

With the object of obtaining some further insight into its constitution, gossypitol tetraethyl ether, 3.84 grams dissolved in a solution of 2 grams of potassium hydroxide in 384 c.c. of water, was gradually treated at 5° with 2 grams of potassium permanganate in 100 c.c. of water. Oxidation readily took place, and at the end of the operation the mixture was heated on the steam-bath, filtered, and the clear liquid evaporated to a small hulk. By treatment with carbon dioxide and extraction with ether, 0.75 gram of the attacked ketone was recovered. The solution when now neutralised with acid became cloudy, and yielded to ether a pale brown, acid substance; this was extracted with boiling benzene, the liquid evaporated, and the crystals which had separated after keeping for some days were collected. The yellow, crystalline powder (0.27 gram) was digested with some quantity of boiling water, whereby a trace of an orange-coloured, resinous impurity remained undissolved; and on cooling pale yellow needles were deposited (*A*), whereas a further quantity was obtained on concentrating the liquid (*B*). Only 0.175 gram of this compound was available for analysis:

0.0981 gave 0.2016  $CO_2$  and 0.0546  $H_2O$ . C=56.05; H=6.18;

Et=28.83.

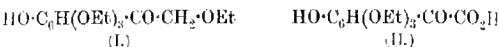
0.0720 gave 0.1682 AgI

$C_{11}H_{15}O_6$  requires C=56.37; H=6.04; Et=29.19 per cent.

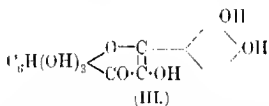
This acid, for which the name *gossypatonic acid* is suggested, although here described as a pale yellow substance, is probably in reality colourless, but sufficient material was not available to ascertain if this was certainly the case. Both fractions *A* and *B* melted at 151–155°, with evolution of gas.



As gossypitol (tetraethyl ether,  $C_{16}H_{24}O_6$ , is soluble in potassium hydroxide solution it contains a free hydroxyl group, and as it yields an oxime, and further possesses four ethoxy-groups, all the oxygen atoms are accounted for. There is accordingly little doubt, therefore, that its constitution is as follows (I):



and, again, the analytical figures of gossypetic acid harmonise with this view, as they are in agreement with those required by a *hydroxytriethoxybenzeneglyoxylic acid* (compare Herzig, *Monatsh.*, 1891, **12**, 187). The results, therefore, of the hydrolysis of gossypetin hexaethyl ether with alcoholic potassium hydroxide suggest that it possesses the flavonol constitution (III), as, indeed, its general properties also indicate.



A remarkable resemblance is thus to be observed between gossypetin and quercetagenin (T., 1913, **103**, 219), in that both are hexahydroxyflavones, containing in each case tetrahydroxybenzene and catechol nuclei.

The melting point of gossypetin about which some uncertainty existed owing to the blackening of the tube, and which was considered (*loc. cit.*) to be about  $300^\circ$ , is now found to be in reality  $311\text{--}313^\circ$ . For the reason indicated the exact point is not apparent, and to be certain that fusion had occurred, the breaking of the tube was necessary.

#### *An Oxidation Product of Gossypetin.*

As previously stated (*loc. cit.*), gossypetin is readily susceptible to oxidation in alkaline solution, the liquid passing through brown, orange, and green to deep blue, and it was interesting to determine the cause of this colour change. The deep blue solution on acidification becomes red, and if concentrated deposits a reddish-brown precipitate, which on gentle warming usually becomes crystalline. That this reaction is not deep-seated appears evident, for when the acid mixture is treated with sodium hydrogen sulphite solution a reversion into yellow gossypetin quickly takes place, and the reoxidation of this with air and subsequent reduction can be performed *ad libitum*. A second method consists in adding alcoholic potassium hydroxide to an alcoholic solution of the coloured matter, the precipitated potassium salt rapidly becoming blue

coloured, and this is collected, dissolved in water, and the clear blue liquid treated with acid. Other oxidising agents were experimented with, and eventually *p*-benzoquinone was selected as being most convenient. A solution of 0.5 gram of gossypetin dissolved in 8 c.c. of absolute alcohol was treated when cold with 0.2 gram of *p*-benzoquinone with agitation, causing the development of a deep reddish-brown coloration. On keeping for a few minutes minute crystals commenced to separate, and the mixture was then heated to 50° until a semi-solid mass was obtained. The product, after being collected and washed with boiling alcohol, weighed 0.127 gram, and in other experiments the yield averaged 90 per cent.

Found: C=56.90, 57.02; H=2.74, 2.79.

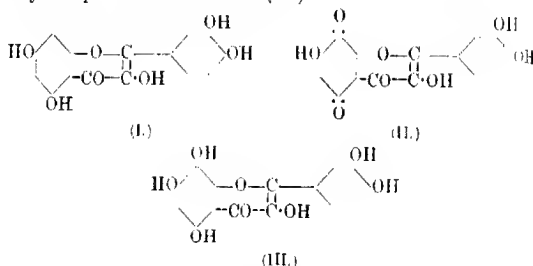
$C_{15}H_8O_8$  requires C=56.96; H=2.53 per cent.

*Gossypitone*, the name proposed for this substance, consists of microscopic needles having a dull red or maroon colour, and, indeed, closely resembles amorphous phosphorus in appearance. It is insoluble in cold water, boiling alcohol, or nitrobenzene, sparingly soluble in boiling water, but readily so in pyridine or quinoline, although apparently it cannot be crystallised from the two latter solvents. Dilute alkalis dissolve it with a pure blue coloration, and when acidified a red liquid is produced in very dilute solutions, but a solution of the dried substance in concentrated sulphuric acid is dull brown. In order to reconvert the gossypitone into gossypetin, 0.8 gram of the former in 200 c.c. of boiling water was treated with 10 c.c. of concentrated sodium hydrogen sulphite solution. The yellow solution on acidification deposited 0.765 gram of minute needles, which on acetylation gave acetyl-gossypetin, melting at 228–230°. (Found: C=56.90; H=1.06.  $C_{15}H_4O_8(Ac)_6$  requires C=56.84; H=3.86 per cent.)

The latter experiment indicates that gossypitone is not a quinhydrone, but a quinone, and the fact also that it is reduced in the cold by phenylhydrazine with brisk evolution of nitrogen fully supports this view. The behaviour of gossypetin is indeed similar to that of excoecarin (T., 1902, **81**, 214).  $C_{13}H_{12}O_6$ , a colouring matter of green ebony, which with bromine and apparently also by means of *p*-benzoquinone yields the green excoecarone,  $C_{12}H_{10}O_6$ , to which the tint of green ebony on keeping is no doubt due. With sulphurous acid it is at once reconverted into excoecarin, and as the latter contains a quinol or toluquinol nucleus, excoecarone is thus probably a paraquinone.

Wheldale (*Report to the Evolution Committee of the Royal Society*, 1909, **5**, 1), as a result of experiments with *Antirrhoeum*,

*majus*, has made the interesting suggestion that anthocyanin (in this case the magenta anthocyanic pigment) "may be regarded as an oxidation product of a chromogen in nature allied to the series of flavone colouring matters; the oxidation is brought about probably through the agency of an oxydase." Evidence for this hypothesis is derived by this author from results obtained in cross-breeding with varieties of *Antirrhinum majus*, and is also given in other papers; moreover, in the *Biochemical Journal* (1913, 7, 85), the matter is further elaborated, and it is considered that anthocyanin includes many substances, "having in general similar properties, but differing among themselves as regards constitution," and "would occur as glucosides." Nierenstein and Wheldale (*Ber.*, 1911, 44, 3487), again, have oxidised quercetin (I) with chromic acid, and obtained quercetone, a red substance soluble in alkali with a blue colour, for which the constitution (II) is suggested. This latter compound, considered by these authors to consist possibly of an anthocyanin by simultaneous acetylation and reduction, yields the acetyl compound of the flavonol (III):



\* Anthocyanin, or cyanin, according to Frémy and Cloez (*J. pr. Chim.*, 1854, 62, 629), is an amorphous, blue powder present in flowers. With acids it gives a red with alkalis a green, colour, and is decolorised by reducing agents, though the latter returns on exposure to air. These authors consider that the red colour of flowers, this compound, reddened by the acidity of vegetable juice. On the other hand anthocyanin appears to be generally regarded by botanists as the red colour of flowers turning blue with alkali, although Weigert (compare Wheldale, *Proc. L. Soc.*, 1909, B, 81, 44) again describes two classes of anthocyanin, "vermillion" and "rhubarb," the former giving, with basic lead acetate, bluish-green, and the latter red precipitates. Wheldale (*Report to Evolution Committee, loc. cit.*) also includes among the anthocyanines, a "pigment" present in the "Rose Doré" variety of *Antirrhinum majus*, which is not turned blue by alkali, so, consequently, it would appear that the term "anthocyanin" refers to the red colouring matter of any flower. According to Molisch (*Bot. Zeit.*, 1905), anthocyanin frequently exists in the cell in a crystalline condition, and Wheldale has isolated, from a variety of the *Antirrhinum majus*, a crystalline magenta "pigment" which decomposes when heated to 340 (*Biochem. J.*, *loc. cit.*).

The properties assigned to quercetone resemble those possessed by gossypitone, but although little doubt appears to exist that they should be closely allied, the fact that the former gives with concentrated sulphuric acid a red solution is proof that they cannot be identical. Moreover, the flavonol (III) is not gossypetin, for it melts at 352–359°, and its hexamethyl ether at 147–149°.

That the anthocyanin of certain flowers arises from the production of a flavone-quinone or of its glucoside seems plausible, although such being the case it appears open to conjecture whether the quinone, as in the above example, is derived directly from the quercetin, or whether the quinol itself (or other flavone readily susceptible to quinonoid transformation) is synthesised in the plant without an intermediate quercetin stage. Flavone colouring matters rarely exist singly in flowers, although frequently owing to its small amount the presence of the second constituent of this class is not always apparent. Purified preparations of quercetin and other flavonols when exposed to air frequently develop a more or less green tint, and special mention in this respect may be made of rutin prepared by the usual methods, either from rose petals or the flower buds of *Sophora japonica*. Such a behaviour indicates the presence of a trace of an otherwise unsuspected colouring matter, which is readily oxidisable, and possibly, therefore, the parent of an anthocyanin. Although experiments are incomplete, it is probable that *p*-benzoquinone in alcoholic solution will prove a useful reagent for the detection of traces of such compounds in flavone preparations, by the development of a reddish-brown tint, which will be pale or otherwise according to circumstances. Observations hitherto carried out are promising in this respect, and indicate that with pure flavonols no reaction of this character occurs.

Gossypitone possesses strong dyeing properties, and gives the following shades with mordanted woollen cloth :

Chromium.	Aluminium.	Tin.	Iron.
Dull brown.	Orange-brown.*	Orange-red.	Deep olive.

\* On mordanted calico the shade is greenish-brown.

These, it is interesting to note, are identical with those given in these circumstances by gossypetin itself, and it is accordingly evident that during this dyeing operation oxidation of the latter to gossypitone takes place. The dyeing experiments with gossypetin are described in a previous communication (*loc. cit.*).

Although the flowers of the ordinary Indian cotton plant are yellow, other varieties are to be met with, such as those of the *S. arboreum*, which are of a red colour. In a lengthy paper,

"Studies on Indian Cotton" (*Journal of Genetics*, 1911, 1, 107), by H. M. Leake, special reference to this anthocyanic pigment occurs, and it is pointed out that in plants of the type *G. arboreum* and *G. sanguineum* its presence communicates an intense red to the entire plant (stem, leaves, and flowers). Owing to the kindness of Mr. Leake, a supply of these red petals has been available for examination, and there can be no doubt that these also contain gossypetin as glucoside. The fact that gossypetin can be readily converted into red gossypitone provides at first sight a simple explanation of the origin of the red colour of this variety of flower but although in a sense this may be partly correct, it is doubtful whether gossypitone exists as such, at least in the freshly gathered petal.

A point of importance in regard to anthocyanin, and to which botanists do not appear to have called attention, is the fact, borne out by numerous dyeings in this laboratory with freshly gathered flowers, that towards mordanted fabrics it behaves as a fugitive, green or greenish-blue colouring matter.<sup>2</sup> Most probably it is a blue dyestuff, the shade in these instances being modified by the presence of flavone glucosides, although apparently owing to the very elastic definition applied by botanists to these products a hard and fast rule on this point is impossible.

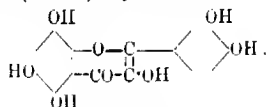
Employing mordanted calico, air-dried red cotton-flower petals, however, give the anticipated green "anthocyanic" shade, or at least a much greener shade than that produced by the yellow variety, whereas in case free gossypitone had been present a brownish-yellow shade should have resulted. That anthocyanins, as indeed Wheldale (*loc. cit.*) has suggested, are glucosides seems certain owing to their ready solubility, and an experiment was now carried out to determine if gossypitone could be prepared in a similar form.

The result of a preliminary investigation of the Indian cotton flowers has shown that they contain the gossypetin or at least part of it in the form of a glucoside sparingly soluble in hot water. This compound gives an acetyl compound melting at 239–242°, but whether it is in reality the gossypitrin formerly isolated from the Egyptian variety or a modification of it has not yet been decided. A solution of this substance in dilute alcohol when treated with a little *p*-benzoquinone in the cold, became brownish-red, and gradually deposited a gelatinous, maroon-coloured precipitate similar to gossypitone. On heating the mixture the substance became crystalline, and when collected, washed with alcohol, and dried formed a gl' shining mass of reddish-violet needles. Although

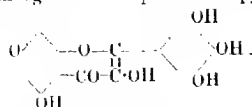
<sup>2</sup> Nierenstein and Wheldale have not described the dyeing properties of their quercetone.

at first sight it seemed evident that here was a glucoside of gossypitone; this is by no means certain in that its alkaline solutions are not blue but orange-yellow. Very interesting, however, are the dyeing results given by this glucoside; for employing mordanted calico it yields bright green shades, which are the cumulative effect of a blue and yellow colouring matter, into which it appears to be converted by the action of the boiling water. Owing to the fugitive character of the blue dye, this gradually disappeared on exposure to the laboratory atmosphere for a few days, a yellow pattern thus resulting. These preliminary results are here given because as the preparation of the gossypetin glucoside is laborious the explanation of this reaction must occupy a considerable time.

Until a definite knowledge of the tetrahydroxybenzene nucleus present in gossypetin has been obtained, the position of the hydroxyl groups in this portion of the molecule can only be conjectured. Existing as it does side by side with quercetin, it seems natural to consider that gossypetin is a hydroxyquercetin. Again, should gossypitone be a *p*-quinone, the constitution of gossypetin will be the same as that which Nierenstein and Wheldale have suggested for the flavonol (*loc. cit.*) which they obtained from quercetone, but the descriptions of the two compounds are not in agreement. On the assumption of the necessity for a quinol nucleus in gossypetin, a second constitution already referred to in connexion with quercetageitin (*loc. cit.*) is possible:



On the other hand, it suggests itself as not unreasonable that gossypitone may eventually prove to be an orthoquinone\*: thus the presence of a pyrogallol grouping in the nucleus in question is very possible, and, if so, would account for the ready oxidation of the alkali salts of gossypetin. Interesting in this respect is the fact recently ascertained that by means of alcoholic *p*-benzoquinone solution pyrogallol gives the compound  $\text{C}_{12}\text{H}_4\text{O}_8$ , possibly hydroxy-*o*-benzoquinone, formerly obtained with *isoamyl* nitrite (T., 1906, 39, 802). Myricetin again, which possesses a pyrogallol nucleus,



\* The reactions of anthocyanin or cyanin given by Feilmy and Coet (*loc. cit.*) suggest that this is very probably an orthoquinone.

behaves very similarly to gossypetin when its alkaline solution is exposed to air (T., 1896, 69, 1287), and preliminary experiments have shown that if this is carried to the blue stage, on acidification a reddish-brown precipitate, apparently of a similar nature to gossypitone and reducible with sulphurous acid, is obtained. Alkaline oxidation with myricetin is, however, difficult to control, as a change from the blue to a reddish-violet stage rapidly occurs, even if the salt is prepared in alcoholic solution, and it is anticipated that the reaction may be troublesome to elucidate. With alcoholic *p*-benzoquinone also myricetin yields a bright scarlet liquid (but no deposit as in the case of gossypetin), and these colour changes, originating in its pyrogallol grouping, may reasonably be inferred to have an orthoquinonoid explanation.

A further investigation of these points is now in progress.

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LXXIV.—*Studies in the Camphoric Series. Part*  
XXXIV. *Configuration of the Eight Oximino*  
*derivatives of Camphorquinone.*

By MARTIN ONSLOW FORSTER.

BENZIL is the model case of a symmetrical  $\alpha$ -diketone in which the configuration of each oximino-derivative has been established. This is due to Beckmann and Köster (*Annalen*, 1893, 274, 1) who, by following the course of a Beckmann transformation applied to the two monoximes and three dioximes, drew conclusions regarding the spacial disposition of the hydroxyl groups relative to the other parts of the molecule.

The discovery of *isonitrosoepicamphor* in two modifications, constituting the third and fourth monoximes of camphorquinone (T., 1912, 101, 1340), thereby completing the series of eight oximino-derivatives from that diketone, invited an attempt to establish the configuration of these materials on the lines of the Hantzsch-Werner hypothesis, because they present the only recorded case in which all the possible derivatives of an unsymmetrical  $\alpha$ -diketone have been isolated.

Owing to the stability of the camphor nucleus, the method of Beckmann and Köster can be applied in only modified form to

the monoximes, and in the case of the dioximes it has been necessary to rely on arguments which, although perhaps appearing less conclusive at first, certainly have the advantage of depending on less drastic transformations. Briefly stated, this part of the investigation has resolved itself into an inquiry as to the identity of the dioximes arising by the action of hydroxylamine on each monoxime, and then, by a process of elimination based on preliminary knowledge of the configuration of the monoximes themselves, deciding the disposition of the hydroxyl groups in the four dioximes. For this purpose it has appeared desirable to repeat much of the earlier work on the dioximes (T., 1903, 83, 514), and by improving the methods of separating these, to determine with greater certainty their relationship to the monoximes.

Beyond giving the following table, in which details regarding more highly purified materials are slightly amended, it is not necessary to recapitulate the information which has been published from time to time concerning the eight oximino-derivatives of camphorquinone, the history of these compounds having been summarised recently:

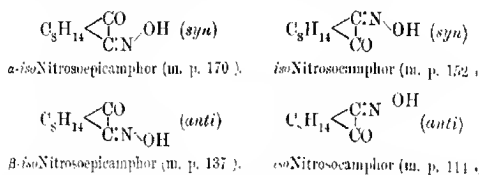
	M. p.	[ $\alpha$ ] <sub>D</sub>	
		Chloroform.	2 per cent. NaOH.
<i>iso</i> -Nitrosocamphor (unstable).....	111°	172.9	275.3
(stable) .....	152	197.0	288.0
<i>iso</i> -Nitrosoepicamphor (unstable) ...	137	179.4	278.5
(stable) .....	170	200.1	422.6
Camphorquinone $\alpha$ dioxime .....	201	51.7	103.8
$\beta$ dioxime .....	248		24.5
$\gamma$ dioxime .....	196	14.1	14.3
$\delta$ dioxime .....	194	52.8	87.0

It must be recalled, however, that the configuration of the two modifications of *isonitrosocamphor* has been established (T., 1905, 87, 232), and the recognition of the stable and unstable forms as *syn*- and *anti*-modifications respectively is the starting point of the present inquiry.

On comparing these isomerides with the third and fourth monoximes of camphorquinone, a similar relationship for the latter suggests itself. The unstable, more readily fusible, more freely soluble, and less optically active *isonitrosoepicamphor* corresponds exactly with the *anti*-monoxime represented by the unstable form of *isonitrosocamphor*, and most probably has, therefore, the *anti*-configuration. This diagnosis is strengthened by the effect of magnesium methyl iodide examined by Dr. Spinner, who has found that the behaviour of unstable *isonitrosoepicamphor* is strictly analogous to that of unstable *isonitrosocamphor*, there being produced a hydroxy oxime which does not yield the anhydride with

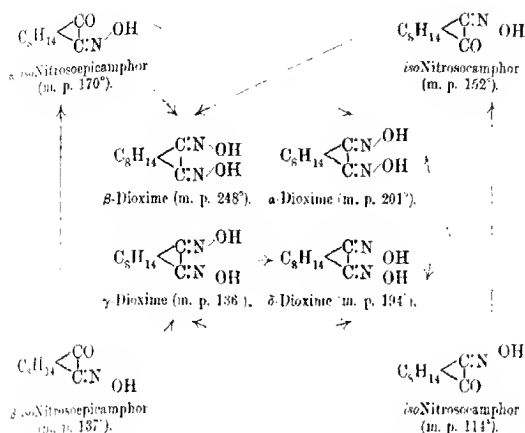


hot alkali, whilst the stable *isonitrosoepicamphor* gives a mixture of the hydroxy-oxime with the anhydride. Moreover, whilst the unstable *isonitrosoepicamphor* may be extracted unchanged from hydrochloric acid (1:2) after boiling the latter during one minute, the stable modification is largely transformed into  $\beta$ -camphornitrilic acid. It is reasonable, therefore, to represent the four monoximes of camphorquinone in the manner following:



Passing now to the dioximes, it is at once noticeable that the  $\gamma$ -modification possesses in marked degree the characteristics associated with the *anti*-monoximes; it dissolves much more freely in organic media, melts at a far lower temperature, and has lower specific rotatory power than the three isomerides, into one of which ( $\delta$ ) it passes when heated. Being the only dioxime convertible into another, resembling in this respect the *anti*-monoximes, and displaying the attributes indicated above, it is natural to conclude that the *anti*-configuration prevails in the  $\gamma$ -dioxime, and as the greatest contrast is presented by the  $\beta$ -dioxime, it seems reasonable to regard the latter as the *syn*-modification. The two *amphic*-configurations are thus left for the  $\alpha$ - and  $\delta$ -dioximes, and in considering how these may be apportioned, cognisance must be taken of the fact that the *anti*-modification of *isonitrosoepicamphor* is more stable than the corresponding derivative of *isonitrosocamphor*, whence it follows that, since the change in configuration on passing from the  $\gamma$ -dioxime to the  $\delta$ -isomeride is restricted to a single oximino-group, that group is the one present in *isonitrosocamphor*.

The foregoing hypothesis has been submitted to a practical test by ascertaining, in the case of each dioxime, which monoxime-*s* are involved in its production. The results of this test, which are embodied in the following diagram, support the hypothesis in every particular; in fact, no one among the numerous observations which have been made in connexion with these compounds will be found in conflict with the suggestions here made as to their configuration.



Furthermore, it is worth remarking that a qualitative relationship in respect of specific rotatory power among the dioximes may be calculated in the following manner:

$$\begin{aligned}
 \alpha\text{-Dioxime} &= \frac{1}{2}[\text{isoNitroso-camphor (anti)} + \text{isomnitroso-camphor (syn)}] \\
 &= \frac{1}{2}(275.3 - 422.0) = -73.3^\circ \\
 \beta\text{-Dioxime} &= \frac{1}{2}[\text{isoNitroso-camphor (syn)} + \text{isomnitroso-camphor (anti)}] \\
 &= \frac{1}{2}(288.0 - 422.0) = -67.0^\circ \\
 \gamma\text{-Dioxime} &= \frac{1}{2}[\text{isoNitroso-camphor (anti)} + \text{isomnitroso-camphor (anti)}] \\
 &= \frac{1}{2}(275.3 - 278.5) = -1.6^\circ \\
 \delta\text{-Dioxime} &= \frac{1}{2}[\text{isoNitroso-camphor (syn)} + \text{isomnitroso-camphor (anti)}] \\
 &= \frac{1}{2}(288.0 - 278.5) = +4.7^\circ
 \end{aligned}$$

This is in qualitative agreement with the facts so far as (1) the  $\alpha$  and  $\beta$ -dioximes are both levorotatory, (2) the  $\alpha$ -dioxime has a higher rotatory power than the  $\beta$ -modification, (3) the  $\gamma$ -dioxime has the lowest rotatory power of all, and (4) the  $\delta$ -dioxime is dextro-rotatory. The above calculation is based on the values in alkali because the  $\delta$  dioxime is so very sparingly soluble in organic media.

Without going into unnecessary details it may be stated that alternative relationships between the eight oximino-derivatives of camphorquinone have been considered, but these have been found, as some cardinal point or other, to be in direct conflict with experimental observation.

## EXPERIMENTAL.

*Separation of isoNitrosocamphor (m. p. 152°) from the Claisen Mixture.*

One hundred grams of the mixture were dissolved in 300 c.c. of ether and treated with the ferric chloride dissolved from 90 grams by 500 c.c. of ether; an intense, brownish-red coloration was immediately developed, and after an interval of twelve hours the solvent was allowed to evaporate in a current of air. On filtering the treacly residue there remained a crystalline paste, which was drained on porous earthenware, suspended in water, washed on the filter, and dissolved in 5 per cent. sodium hydroxide; a small quantity of ferric hydrate having been filtered, dilute sulphuric acid precipitated the *isonitroso*-derivative in crystals instead of an oil. Recrystallisation from dilute methyl alcohol gave 50 grams of the stable modification quite free from the isomeride. The original mother liquor was a viscous, dark brown oil, yielding a crystalline product when shaken with water; it was hoped that this might consist of the unstable modification, but proceeding as above, an additional 30 grams of the stable isomeride was obtained. This portion was far from pure, but was suitable for the preparation of aminocamphor.

The action of ferric chloride in this process is somewhat obscure, as the amount of iron in the crystalline residue deposited from the ether is insufficient for a ferric derivative analogous to the metallic compounds obtained by Francesconi and Piazza (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 128) from the Claisen mixture and silver nitrate or mercurous nitrate. Nevertheless, it has the effect which solvents fail to accomplish.

*Action of Hydroxylamine on the Claisen Mixture.*

The facility with which the unstable modification of *isonitroso*-camphor is transformed into the isomeride made it desirable to study the action of hydroxylamine in cold solutions, so that the maximum of dioxime from the former might be isolated.

Fifty grams of the Claisen mixture dissolved in 250 c.c. of alcohol and treated with a solution containing 40 grams of hydroxylamine hydrochloride and 80 grams of crystallised sodium acetate in 250 c.c. of water formed a clear liquid, from which, after twelve weeks, 40 grams of pale brown crystals had separated. On extracting this material four times with 250 c.c. of boiling acetone, 5 grams of snow-white powder consisting of almost pure  $\beta$ -dioxime remained. Each of the two first extracts deposited

5 grams of pure  $\alpha$ -dioxime, the third yielding 2 grams of  $\alpha$ -dioxime mixed with a very small proportion of  $\beta$ -dioxime, 0.2 gram of the latter being the only deposit from the fourth. On evaporating the acetone mother liquors, the residue weighed 19 grams, almost completely soluble in 400 c.c. of boiling acetone, which deposited 1.3 grams of  $\alpha$ -dioxime on cooling, whilst the filtrate yielded 14 grams of brown residue when evaporated. On extracting this with cold benzene, 12.5 grams of colourless material remained, dissolving in 250 c.c. of boiling ethyl acetate, from which 4.4 grams of  $\alpha$ -dioxime separated; reducing the mother liquor to one-half its original bulk gave 2.2 grams of  $\alpha$ -dioxime mixed with a small proportion of  $\delta$ -dioxime, still further concentration yielding 5 grams of the latter substance. Meanwhile, the mother liquor from the original 40 grams was freed from alcohol on the water-bath, when the yellow, sticky mass which separated was found to leave, on extraction with cold benzene, 7 grams of colourless dioxime, consisting principally of the  $\delta$ -modification. Under the conditions stated, therefore, 50 grams of the Claisen mixture furnished approximately 23 grams of  $\alpha$ -dioxime, 5 grams of  $\beta$ -dioxime, and 12 grams of  $\delta$ -dioxime.

Proceeding as above with the stable modification of *isonitroso*-camphor, and subjecting the product to systematic fractionation, the only dioximes isolated were the  $\beta$ - and  $\delta$ -isomerides, whence it follows that the  $\alpha$ -dioxime, which formed the major product from the Claisen mixture, must arise from the unstable *isonitroso*-camphor present in that material.

The action of hydroxylamine in alkaline solution was then studied. 100 grams of hydroxylamine hydrochloride dissolved in water being added to an alkaline solution containing 100 grams of the Claisen mixture and 90 grams of sodium hydroxide, the total volume of water being 1000 c.c. After three weeks the liquid was extracted with ether, and fractionally acidified with dilute sulphuric acid, which precipitated a red, tarry material first, followed by a honey-like gum: as soon as the aqueous liquid failed to develop colour with ferrous sulphate, it was decanted from the precipitate, yielding 24 grams of snow-white  $\gamma$ -dioxime with more acid. The gummy precipitate left 6 grams of  $\gamma$ -dioxime when extracted with cold benzene to remove unaltered *isonitroso*camphor, whilst the tarry material gave 6 grams of  $\delta$ -dioxime as a result of the same treatment. It having been shown already that under these conditions the stable *isonitroso*camphor does not yield the  $\gamma$ -dioxime, it follows that this substance arises from the unstable modification.

The  $\gamma$ -dioxime was recrystallised from methyl alcohol diluted

with a small proportion of water, separating in snow-white needles melting at  $136^{\circ}$ . One per cent. solutions in chloroform, alcohol and 2 per cent. aqueous sodium hydroxide gave  $[\alpha]_D$   $16.4^{\circ}$ ,  $22.7^{\circ}$ , and  $14.3^{\circ}$  respectively.

The  $\delta$ -dioxime has been obtained in condition somewhat purer than that previously described by dissolving 25 grams of the  $\gamma$ -dioxime in 50 c.c. of cold absolute alcohol and heating the solution under reflux during eight hours, when 13 grams of the  $\delta$ -dioxime crystallised on cooling, whilst the mother liquor furnished 8 grams on concentration. Recrystallisation from methyl alcohol diluted with a small proportion of water yielded a specimen melting at  $194^{\circ}$ , giving  $[\alpha]_D$   $52.8^{\circ}$ ,  $80.0^{\circ}$ , and  $87.0^{\circ}$  in chloroform, alcohol, and 2 per cent. sodium hydroxide respectively.

*Action of Hydroxylamine on the iso-Nitroso-derivatives of  
Epicamphor.*

It has been shown (T., 1912, 101, 1353) that with hydroxylamine acetate,  $\alpha$ -isonitrosoepicamphor (m. p.  $170^{\circ}$ ) yields the  $\alpha$ - and  $\beta$ -dioximes, whilst the  $\delta$ -dioxime is the sole product from the  $\beta$ -modification (m. p.  $137^{\circ}$ ).

$\alpha$ -isonitrosoepicamphor (3 grams) dissolved in sodium hydroxide (3 grams) was treated with hydroxylamine hydrochloride (3 grams), the bright yellow solution being diluted to 30 c.c. Within a few minutes the colour had perceptibly faded, and during three days, massive, transparent crystals separated, becoming opaque when rubbed with water: this was the sodium derivative of the  $\beta$ -dioxime, yielding nearly 2 grams of that material. The filtrate on acidification gave 0.75 gram of  $\beta$ -dioxime mixed with a small proportion of the  $\alpha$ -modification.

When  $\beta$ -isonitrosoepicamphor was treated in the same way, the colour faded rapidly, but crystals did not separate. Fractional precipitation with dilute sulphuric acid gave (1) 1.5 gram of  $\gamma$ -dioxime mixed with  $\delta$ -dioxime in the proportion of 2:1, and (2) 1.5 grams of almost pure  $\gamma$ -dioxime: thus the principal product is the  $\gamma$ -dioxime, with about 15 per cent. of the  $\delta$ -modification.

*Action of Magnesium Methyl Iodide on iso-Nitrosoepicamphor.*

An ethereal solution of  $\beta$ -isonitrosoepicamphor (3 grams) was added slowly to the well-cooled Grignard agent from 1.2 gram of magnesium and 7.5 grams of methyl iodide, the product after twelve hours being decomposed with ice and acetic acid. The ethereal liquid having been extracted four times with 10 c.c. of 5 per cent. sodium hydroxide solution to remove unchanged im-

nitrosoepicamphor, a crystalline residue was left on evaporation; after being recrystallised three times from dilute alcohol, the colourless needles melted at 96°:

0.1365 gave 0.3227 CO<sub>2</sub> and 0.1191 H<sub>2</sub>O. C = 64.48; H = 9.76.

0.1631 „ 10.0 c.c. N<sub>2</sub> at 22° and 758 mm. N = 6.96.

0.2836 lost 0.0128 at 100°. H<sub>2</sub>O = 4.51.

C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>N requires C = 66.95; H = 9.71; N = 7.11 per cent.

C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>N,  $\frac{1}{2}$  H<sub>2</sub>O requires C = 64.02; H = 9.78; N = 6.80;

H<sub>2</sub>O = 4.37 per cent.

The substance is readily soluble in organic media, including hot petroleum, but is insoluble in water. It is amphoteric, and whilst the alkaline solution remains clear when boiled, the acid solution rapidly becomes turbid when heated, doubtless owing to the transformation:



just as in the case of the  $\beta$ - and  $\gamma$ -modifications of the corresponding derivative from isonitroso-camphor (T., 1905, 87, 232).

When  $\alpha$ -isonitrosoepicamphor was treated in the same way the ethereal liquid yielded with sodium carbonate  $\beta$ -camphornitrilic acid, which was not produced from the isomeride; after unchanged material had been removed with sodium hydroxide the solvent deposited a viscous oil, which did not crystallise during many weeks in the desiccator. Analysis indicated a mixture of the expected oxime with its anhydride, and this fact, in conjunction with the production of  $\beta$ -camphornitrilic acid, may be taken as suggesting the *syn*-configuration for  $\alpha$ -isonitrosoepicamphor.

I desire to express my indebtedness to Dr. H. Spinner for his valuable assistance in connexion with the two modifications of isonitrosoepicamphor.

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# LXXV.—*Externally Compensated Hydroxyhydrazino-hydrindene, its Derivatives, and Resolution into Optically Active Components.*

By DAVID HENRY PEACOCK

IN spite of the interest attaching to the resolution of externally compensated aldehydes and ketones, very few optically active hydrazines have been prepared, and in no case has a racemic

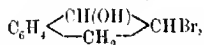
hydrazine been resolved into its optically active components. Neuberg and Federer (*Ber.*, 1905, **38**, 866) introduced the optically active amyl group into phenylhydrazine, and so obtained an active hydrazine; Kijner (*J. pr. Chem.*, 1895, [ii], **52**, 424) prepared menthonomenthylhydrazine from active bromomenthylamine, and from it, by hydrolysis, the corresponding menthylhydrazine.

Bromohydroxyhydrindene has already (Pope and Read, *T.*, 1912, **101**, 758) been converted smoothly and in quantity into the corresponding amine, hydroxyhydrindamine, which is a crystalline compound, forming easily crystallisable salts and derivatives, and is readily resolvable into its optically active components. It was therefore expected that the corresponding hydrazine compound would exhibit similar properties and be resolvable into stereoisomerides, which could then be used for the resolution of externally compensated aldehydes and ketones.

Hydroxyhydrazinohydrindene has the disadvantage of being somewhat unstable in the free state. Its salts when pure and dry are stable, but solutions of them cannot be evaporated to dryness on a water-bath without yielding a considerable quantity of a dark red solid, which melts at 182° and is insoluble in water; solutions can, however, be concentrated to a considerable extent by boiling under diminished pressure, 100 mm. and less, without very appreciable decomposition.

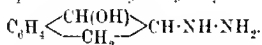
#### EXPERIMENTAL.

Externally compensated 2-bromo-1-hydroxyhydrindene,



was prepared by the method of Pope and Read (*T.*, 1912, **101**, 760), and the product, after thorough extraction with light petroleum, was dried and used without further purification.

*Externally Compensated 1-Hydroxy-2-hydrazinohydrindene.*



The best method of preparing this substance appears to be the following. Bromohydroxyhydrindene (50 grams) is mixed with hydrazine hydrate (50 grams) in a flask fitted with a reflux condenser, and gradually heated in an oil-bath. The mixture becomes quite liquid at 90—100°, and a reaction soon sets in so vigorously that the flask has sometimes to be cooled; when the initial vigour has abated, the flask is heated at 135—145° for two hours, and the excess of hydrazine hydrate distilled off under diminished pressure from a water-bath. The residue, when cooled, sets to a solid mass

(70 grams), which, when extracted with warm water, leaves a small quantity of insoluble residue, melting at 202–204°, and consisting of the condensation product of two molecules of bromohydroxyhydrindene with one of hydrazine. The aqueous extract is treated with solid potassium hydroxide (30 grams), and the mixture left to remain all night in a cooled exhausted vessel. The base (about 30 grams) separates as a granular solid, is filtered off through muslin, and is recrystallised from a large quantity of boiling benzene, in which it is moderately soluble. It is very sparingly soluble in cold benzene, chloroform, or ether, insoluble in light petroleum, and readily soluble in alcohol or water. It crystallises in colourless scales, melting at 87–88°, and decomposes on keeping even in an exhausted sealed tube. The following analyses were obtained with material that had been preserved two days and three days respectively:

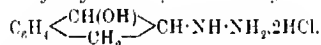
(1) 0.188 gave 0.443 CO<sub>2</sub> and 0.124 H<sub>2</sub>O. C=64.2; H=6.6.

(2) 0.145 „ 0.338 CO<sub>2</sub> „ 0.098 H<sub>2</sub>O. C=63.6; H=7.5.

C<sub>9</sub>H<sub>12</sub>ON<sub>2</sub> requires C=65.8; H=7.3 per cent.

When carbon dioxide is passed into benzene or alcoholic solutions of the base a carbonate is precipitated.

*dl-1-Hydroxy-2-hydrazinohydrindene Hydrochloride,*



This salt is precipitated on mixing alcoholic solutions of the base and hydrogen chloride, and may be prepared more directly by the following process.

Bromohydroxyhydrindene (40 grams), hydrazine hydrate (20 grams), absolute alcohol (50 grams), and pure quick-lime (20 grams) are mixed and shaken for three days in a stoppered bottle; the product is extracted with boiling absolute alcohol, filtered, cooled, and, if necessary, filtered again. Dry hydrogen chloride is then passed for some time into the cooled solution, and after remaining for two hours, the precipitated hydrochlorides are collected and extracted with a boiling mixture of benzene and alcohol, which leaves hydrazine hydrochloride undissolved; the hydrochloride of the organic base separates readily on allowing this extract to cool. The salt is readily soluble in hot absolute alcohol and water, but sparingly so in cold alcohol, boiling benzene, and ethyl acetate; it crystallises in colourless scales, melting at 165°. It contains two molecules of hydrochloric acid to one of the base, and these are retained even on recrystallisation from water. The aqueous solution does not yield a solid platinumchloride with chloroplatinic acid, but



gives a white precipitate with mercuric chloride; it very readily reduces copper sulphate solution:

0.1026 gave 0.1663  $\text{CO}_2$  and 0.0542  $\text{H}_2\text{O}$ .  $\text{C}=44.2$ ;  $\text{H}=5.7$ .

0.1961 " 0.2302  $\text{AgCl}$ .  $\text{Cl}=29.1$ .

$\text{C}_6\text{H}_{12}\text{ON}_2 \cdot 2\text{HCl}$  requires  $\text{C}=45.6$ ;  $\text{H}=5.9$ ;  $\text{Cl}=29.9$  per cent.

If the reaction mixture obtained by shaking as above described is extracted with boiling ethyl acetate or benzene, a crystalline precipitate is formed on cooling which crystallises from alcohol or ethyl acetate in white, shining scales, melting at  $255^\circ$ ; this substance is a double compound of the hydrazine with calcium bromide:

0.1542 gave 0.1075  $\text{AgBr}$ .  $\text{Br}=29.7$ .

0.1351 " 0.0928  $\text{AgBr}$ .  $\text{Br}=29.2$ .

$(\text{C}_6\text{H}_{12}\text{ON}_2)_2 \cdot \text{CaBr}_2$  requires  $\text{Br}=30.3$  per cent.

The sulphate,  $(\text{C}_6\text{H}_{12}\text{ON}_2)_2 \cdot \text{H}_2\text{SO}_4$ , is precipitated on mixing an alcoholic solution of the base with twice the calculated quantity of alcoholic sulphuric acid. It crystallises from hot dilute alcohol or water in colourless, hexagonal plates, melting and decomposing at  $224^\circ$ :

0.0987 gave 0.0531  $\text{BaSO}_4$ .  $\text{SO}_4=22.1$ .

$\text{C}_6\text{H}_{12}\text{O}_2\text{N}_4\text{S}$  requires  $\text{SO}_4=22.5$  per cent.

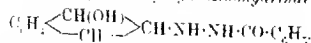
The oxalate,  $\text{C}_6\text{H}_{12}\text{ON}_2 \cdot (\text{CO}_2\text{H})_2$ , separates on mixing alcoholic solutions of equivalent proportions of the free base and oxalic acid; after recrystallisation from hot alcohol it is obtained in colourless needles, melting at  $173^\circ$ . It is readily soluble in water, but sparingly so in most organic solvents, except boiling rectified spirit. In both this salt and the hydrochloride the base is diacidic, whereas in the sulphate it is monacidic:

0.1660 gram gave 16.67 c.c.  $\text{N}_2$  (moist) at 18 and 762 mm.  $\text{N}=11.6$ .

$\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2$  requires  $\text{N}=11.1$  per cent.

The *d*-camphor- $\beta$ -sulphonate and *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate prepared in a manner similar to the above were with difficulty obtained in a crystalline condition, owing to their hygroscopic character; they decomposed on keeping, becoming dark red.

*di-1-Hydroxy-2-benzoylhydrazinohydrindene*,



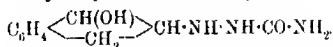
The benzoyl derivative prepared from the hydrochloride by the ordinary Schotten-Baumann process crystallises from a mixture of alcohol and acetone in small white nodules, melting at  $196^\circ$ . Benzoylation in pyridine solution with two molecules of benzoyl chloride yielded only the monobenzoyl derivative:

0.1181 gave 0.3010  $\text{CO}_2$  and 0.0620  $\text{H}_2\text{O}$ .  $\text{C}=69.4$ ;  $\text{H}=5.9$ .

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{C}=71.6$ ;  $\text{H}=5.9$  per cent.

The hydrochloride when heated with acetic anhydride yielded an oil which could not be caused to crystallise; bromohydroxyhydrindene behaves in the same way. The benzenesulphonyl- and *p*-toluenesulphonyl derivatives could not be prepared by the ordinary Schotten-Baumann process, black, uncrystallisable resins being produced.

*dl-1-Hydroxy-2-semicarbazinohydrindene,*

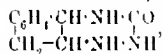


This compound is obtained in quantitative yield when aqueous solutions of equimolecular proportions of the hydrochloride of the base and potassium cyanate are mixed and left to remain for an hour; it separates as a white, amorphous powder, which crystallises from hot spirit in minute scales, melting at  $195^\circ$ . It dissolves sparingly in most organic solvents, in water or dilute acid, and is moderately soluble in hot alcohol, benzene, or concentrated hydrochloric acid; it is very stable, and its solutions can be evaporated to dryness without decomposition:

0.1255 gave 21.4 c.c.  $\text{N}_2$  (moist) at  $20^\circ$  and 758 mm.  $\text{N}=19.4$ .

$\text{C}_9\text{H}_{13}\text{O}_2\text{N}_3$  requires  $\text{N}=20.1$  per cent.

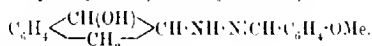
On dissolving the semicarbazide in concentrated sulphuric acid some blackening occurs, but, if the solution is left for two hours and then poured into water and filtered, a yellow solution with a green fluorescence is obtained. This may contain the compound:



and, if so, the hydroxy- and hydrazino-groups in the parent substance are probably in the *cis*-position.

On attempting to prepare the thiosemicarbazide by a similar method no solid separated, and on evaporating the solution the main product was the thiocyanate, which crystallises in colourless rosettes, melting at  $112^\circ$ , and turning pink on keeping.

*dl-1-Hydroxy-2-anisylidenhydrazinohydrindene,*



The hydrochloride of the base is dissolved in a solution containing rather more than two molecular equivalents of sodium acetate and a little acetic acid. The calculated weight of anisaldehyde is then

added to the hot solution, which is well shaken and heated in a boiling-water bath for two hours. On cooling, the hydrazone separates as a solid mass, which is collected, washed with ether, and recrystallised first from hot alcohol, and then from hot benzene, from which it separates in small, flat, yellow scales, melting at  $168^{\circ}$ :

0.1436 gave 12.6 c.c.  $N_2$  (moist) at  $17^{\circ}$  and 744 mm.  $N=9.97$ .

$C_{17}H_{18}O_2N_2$  requires  $N=9.92$  per cent.

dl-1-Hydroxy-2-cinnamylidenehydrazinohydrindene was prepared in a similar way, but this compound separated in the cold as an orange-yellow solid, which seemed somewhat unstable, and was difficult to purify. It was precipitated as a yellow powder from its alcoholic solution by light petroleum, and melted at  $124^{\circ}$ :

0.1175 gave 0.3328  $CO_2$  and 0.0575  $H_2O$ .  $C=77.3$ ;  $H=5.5$ .

$C_{18}H_{18}ON_2$  requires  $C=77.7$ ;  $H=6.4$  per cent.

dl-1-Hydroxy-2-benzylidenehydrazinohydrindene was prepared similarly to the anisic compound; it crystallises from hot rectified spirit in small, white needles, melting at  $107^{\circ}$ .

The vanillylidene compound, prepared as above, was very difficult to purify; it was recrystallised from a hot mixture of methyl alcohol and benzene, and separated in small, yellow scales, melting at  $161^{\circ}$ :

0.1316 gave 10.67 c.c.  $N_2$  (moist) at  $16^{\circ}$  and 746 mm.  $N=9.28$ .

$C_{17}H_{18}O_2N_2$  requires  $N=9.39$  per cent.

The salicylidene compound prepared similarly crystallised from hot spirit in shining, yellow scales, melting at  $213^{\circ}$ .

The piperonylidene compound was, like that of vanillin, very difficult to purify; it was recrystallised several times, and finally separated from benzene in yellow scales, melting at  $201^{\circ}$ :

0.1053 gave 8.6 c.c.  $N_2$  (moist) at  $17^{\circ}$  and 755 mm.  $N=9.58$ .

$C_{17}H_{16}O_2N_2$  requires  $N=9.46$  per cent.

The nitropiperonylidene compound was easily prepared in a very good yield by the usual method. It was recrystallised twice from hot rectified spirit, and obtained in orange-red needles, melting at  $142^{\circ}$ :

0.1590 gave 16.67 c.c.  $N_2$  (moist) at  $20^{\circ}$  and 758 mm.  $N=11.9$ .

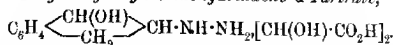
$C_{17}H_{15}O_3N_3$  requires  $N=12.3$  per cent.

The benzylmethylene compound prepared in the usual manner was obtained in a very poor yield; after precipitation by light petroleum from its solution in rectified spirit, it melted at  $96^{\circ}$ .

Neither dextrose nor levulose precipitated hydrazones on being treated in the above manner, nor when left in contact with an alcoholic solution of the free base. An attempt to prepare an

osazone by the usual method only yielded tarry decomposition products.

*1-Hydroxy-2-hydrazinohydrindene d-Tartrate,*



On mixing an alcoholic solution of the externally compensated, hydrazine, which had been recrystallised from benzene, with an alcoholic solution of the equimolecular proportion of *d*-tartaric acid, the *d*-tartrates were precipitated, being almost insoluble in rectified spirit. After five recrystallisations from boiling aqueous alcohol, the mixture was found to be resolved, the less soluble component being the salt *lBdA*, containing the *l*-base. This salt is sparingly soluble in cold water, very sparingly soluble in cold alcohol, and readily soluble in hot water and boiling dilute alcohol, from which latter solvent it separates in very fine colourless needles, melting at 195—196°:

0.1002 gave 0.1856 CO<sub>2</sub> and 0.0624 H<sub>2</sub>O. C=50.5; H=6.6.

C<sub>13</sub>H<sub>18</sub>O<sub>9</sub>N<sub>2</sub> requires C=49.6; H=5.7 per cent.

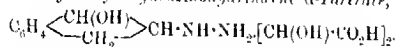
	0.2466 gram in water.			0.2854 gram in water.		
	H <sub>G</sub> green.	H <sub>G</sub> yellow.	N <sub>AgNO<sub>3</sub></sub> .	H <sub>G</sub> green.	H <sub>G</sub> yellow.	N <sub>AgNO<sub>3</sub></sub> .
<i>a</i> .....	0.125°	-0.085°	0°	-0.15°	-0.10°	
[ <i>a</i> ] .....	3.40	2.66	0	3.94	2.62	
[M] .....	12.2	8.34	0	12.4	8.2	

Mean values, [M]: H<sub>G</sub>green = 12.3; H<sub>G</sub>yellow = 8.27°.

Rotatory dispersion: H<sub>G</sub>green/H<sub>G</sub>yellow = 1.48. No mutarotation was observed.

The solutions were made up to 30 c.c., and measured in 4-dcm. tubes at 20°, except where otherwise stated.

*d-1-Hydroxy-2-hydrazinohydrindene d-Tartrate,*



This salt was not obtained in a pure state. On leaving the solutions, from which the more sparingly soluble salt had been separated, to remain, a further crop of crystals was obtained; the less soluble portion was removed from this by fractional recrystallisation, and finally a salt was obtained, melting at 168—169°, this being unchanged by further recrystallisation. The following rotations were observed with two specimens prepared in this way:

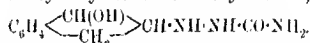
	0.177 gram in water.		0.320 gram in water.	
	H <sub>G</sub> green.	H <sub>G</sub> yellow.	H <sub>G</sub> green.	H <sub>G</sub> yellow.
<i>a</i> .....	-0.60°	-1.16°	-1.05°	
[ <i>a</i> ] .....	25.4	27.2	24.6	
[M] .....	79.8	85.4	75.9	

0.1791 gave 0.3200  $\text{CO}_2$  and 0.0945  $\text{H}_2\text{O}$ .  $\text{C}=48.7$ ;  $\text{H}=5.8$ .

$\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}_2$  requires  $\text{C}=49.6$ ;  $\text{H}=5.7$  per cent.

The resolution by means of tartaric acid could not be effected by the equilibrium method. On dissolving one molecular proportion of the tartrate and of the hydrochloride in hot water or hot dilute alcohol and allowing the solution to cool, the first crystals that separated contained both salts, *lBd.H* and *dBd.H*, and the hydrochloride recovered from the solution showed only a very slight activity.

*1-1-Hydroxy-2-semicarbazinohydrindene*,



The compound separated on mixing warm aqueous solutions of the active tartrate and potassium cyanate; it was recrystallised from rectified spirit, and obtained in shining scales, melting at  $196^\circ$ .

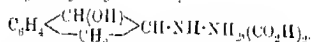
0.1202 gave 0.2515  $\text{CO}_2$  and 0.0633  $\text{H}_2\text{O}$ .  $\text{C}=57.1$ ;  $\text{H}=5.8$ .

$\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}_3$  requires  $\text{C}=58.2$ ;  $\text{H}=5.8$  per cent.

0.1530 gram, in rectified spirit, gave for  $\text{Hg}_{\text{green}}$  light,  $\alpha = 0.39^\circ$ ; whence  $[\alpha] = 14.7^\circ$  and  $[\text{M}] = 28.6^\circ$ .

No mutarotation was observed.

*1-1-Hydroxy-2-hydrazinohydrindene Oxalate*,



The tartrate of the *l*-base was mixed in hot water with the calculated quantity of crystalline barium hydroxide; the precipitated barium tartrate was removed by filtration, the calculated quantity of oxalic acid added, and the solution left to cool. The oxalate then separated in colourless rosettes, melting at  $178^\circ$ ; it crystallises from dilute alcohol in needles:

0.1095 gave 0.2055  $\text{CO}_2$  and 0.0563  $\text{H}_2\text{O}$ .  $\text{C}=51.2$ ;  $\text{H}=5.66$ .

$\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_2$  requires  $\text{C}=51.9$ ;  $\text{H}=5.5$  per cent.

0.1126 gram in water.

	$\text{Hg}_{\text{green}}$	$\text{Hg}_{\text{red}}$	$\text{Na}_{\text{green}}$
$\alpha$ . . . . .	0.33	0.265	0.21
$[\alpha]$ . . . . .	21.98	17.05	13.28
$[\text{M}]$ . . . . .	55.52	44.82	35.54

Rotatory dispersions: 1.24, 1.26.

The rotatory dispersion  $\text{Hg}_{\text{green}}$  vs.  $\text{Na}_{\text{green}}$  is remarkably high; no mutarotation was observed.

The tartrates of the active bases could not be used for the direct preparation of hydrazones, as on heating a solution of the tartrate in presence of sodium acetate and acetic acid with either nitro-

diperaldehyde or anisaldehyde a tarry mass resulted; a similar result was obtained in alcoholic solution. The oxalates would seem to be more suitable for the preparation of the hydrazones.

In conclusion I wish to thank Prof. Pope for suggesting this work, and for the interest he has taken in it.

THE CHEMICAL LABORATORY,  
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# [XXVI.—*The Action of Ozone on Cellulose. Part III.* *Action on Beech Wood (Lignocellulose).*

By CHARLES DORÉE and MARY CUNNINGHAM.

IN a former paper (T., 1912, 101, 503) an account has been given of some experiments relating to the nature of the action of ozone on normal cotton cellulose and the lignocellulose jute.

Of the lignocellulose group, jute represents an elementary type, being an annual growth of comparatively simple structure and composition. In the woods, on the other hand, which are perennial, the changes embodied in the term lignification are of necessity more advanced, and their tissue, although in many respects similar to that of jute, is more complex, both in structure and composition. The results obtained, however, showed that ozone was likely to prove a very suitable reagent for the investigation of such complex natural substances. It has the merit of extreme simplicity—the oxidising system, from a stoicheiometrical point of view, consisting only of oxygen and water, and the reagent, being employed as a diluted gas, is always under perfect control, both as to its concentration and the duration of its action.

In the present communication, therefore, we have extended these observations to the lignocellulose of the woods, beech wood being chosen as a fairly well investigated type. The results obtained have been compared and examined critically in their relation to jute, and finally are discussed in their bearing on the difficult question of the constitution of the lignous complex.

## EXPERIMENTAL.

The very thin beech shavings were steeped in water and treated several times with alcohol in the cold. All weighings were made

on air-dry material, the dry weights given being calculated from the loss in weight of a duplicate sample. Determinations of moisture were made by drying in the water-oven. Water free from air was used throughout.

The ozonised oxygen used had a concentration of about 1.5 grams per 100 grams, or one part (c.c.) per 100 parts (c.c.). Purified and dried oxygen was used, and passed at a rate of 5 to 8 litres per hour through an ozoniser of the Andreoli type. The ozone was found to be absolutely free from oxides of nitrogen.

The constants of the wood substance were determined in the usual way, the copper numbers being estimated by Schwalbe's method ("Chemie der Cellulose," 1911, p. 625). The general method of experiment was the same as that previously described. The shavings were sprayed with water, and packed loosely in tall towers, through which the ozonised oxygen was continuously passed. The carbon dioxide produced in the oxidation was estimated by absorption in barium hydroxide solution and titration with  $N/20$  acid (the results are given as  $N/10$ -acid). The "acidity" of the residual wood was measured by washing the contents of the tower into a beaker and titrating with  $N/10$ -sodium hydroxide solution until neutral to phenolphthalein. After remaining covered for one hour, additional alkali was added until the pink colour returned, and the total quantity used taken as a measure of the acidity developed. Unlike jute, the wood was not bleached by extended treatment with ozone in the presence of water. It was very rapidly attacked, however, absorbing the ozone completely, and after a time became thin and friable. It had a nauseous odour, due to the presence of acids partly volatile in steam.

#### *The Progressive Action of Ozone on Beech Wood in the Presence of Water.*

Quantities of about 2 grams were ozonised for varying periods under comparable conditions. With such quantities, the ozone was always in excess. After titration with  $N/10$ -sodium hydroxide solution, the residue was collected, washed with dilute acetic acid and water, dried, and weighed. The results are given in table I the values previously found for jute being given in brackets. All the figures are calculated on 100 grams of dry substance.

These numbers are very similar to those found for jute. The loss in weight of the beech in the first three hours is exactly the same, namely, 7 per cent. per hour. In the next three hours the rate of loss has fallen to three, and in the last six hours to 1.3 per cent. per hour, compared with 0.7 and 1 per cent. respectively for

TABLE I.  
*Progressive Action of Ozone on Beech Wood.*

Time in hours.	N/10-NaOH. c.c.	CO <sub>2</sub> as N/10 acid. c.c.	Ratio NaOH/CO <sub>2</sub> .	CO <sub>2</sub> weight per cent.	Fibre loss in weight.
1	525 (49.3)	291 (1.46)	1.8	0.65	7.5 (2.5)
3	1926 (149.6)	998 (11.25)	1.9	2.20	21.6 (21.7)
6	3018 (206.0)	1881 (2.300)	1.6	4.15	31.0 (24.4)
12	3320 (27.0)	3140 (3.005)	1.1	6.90	38.9 (30.4)

jute. The lignone reactions were obtainable throughout, but they were weak after twelve hours, and still more so after twenty-four hours (compare T., 1912, 101, 507).

The acidity developed in the substance is produced rapidly and regularly for the first six hours, the amount being roughly 500 c.c. per cent. per hour. In the next six hours, however, the rate has fallen to 50 c.c. per hour. In the case of jute the initial rate is the same, but the marked fall in the rate of production occurs after three hours instead of after six. The carbon dioxide produced is at first very much less than this acidity. For the first six hours it also is uniform and roughly about 300 c.c. per hour. In the final six hours, however, it is still being formed at the rate of 200 c.c. per hour. There is thus an initial rapid production of acidic compounds in the wood substance, which after six hours falls to one-tenth of its value, accompanied by an initially less rapid, but almost uniform production of carbon dioxide, the acidity and the carbon dioxide becoming equal after twelve hours. These results would seem to show that the first effect of the ozone is to attack the less resistant lignone groupings, as was established in the case of jute (*loc. cit.*, p. 506), converting them into acid derivatives. This process continues until about 30 per cent. of the wood substance is found to be removed after neutralisation with N/10-alkali. The ozone then attacks the residual cellulose fibre more slowly, the loss of weight being only 9 per cent. in the final six hours, but continues to oxidise the acid substances first formed, so that the production of carbon dioxide continues uniformly. In order to ascertain what changes had taken place in the wood substance, the following experiments were carried out.

*The Nature of the Products obtained after more Prolonged Treatment with Ozone.*

*Experiment A.*—Twenty grams of fine shavings sprayed with water were submitted to a rapid current of ozone for twenty-four



hours. The whole of the ozone was absorbed by the beech, and to secure uniformity of action the towers were frequently reversed and the contents mixed. The exposure may be regarded perhaps as equivalent to one of fifteen hours only. The shavings became red in places and bleached slightly at the edges, but very little colour change was apparent on drying. The contents of the towers were steeped in water, giving a turbid liquid, which was distilled in a current of steam until acids ceased to distil over.

(i) The distillate measured 5.5 litres, and contained minute floating particles (compare cotton and jute). It required 77 c.c. of  $N/10$ -sodium hydroxide for neutralisation, or 385 c.c. per hundred grams of beech, equivalent to 2.26 per cent. calculated as acetic acid. Qualitative tests indicated the presence of acetic and formic acids as silver nitrate and mercuric chloride were reduced, but as reduction also occurred with ammoniacal silver nitrate some other reducing acid was no doubt present. The distillate also showed a slight reducing power towards Fehling's solution, and gave no reactions indicative of phenols. It gave an amorphous precipitate on warming with phenylhydrazine acetate, which could not be characterised, but on one occasion after treatment with phenylhydrazine needle-shaped crystals separated, which were picked out and found to melt at about  $105^{\circ}$ , agreeing with the melting point of levulinic acid phenylhydrazone. The quantity was too small for investigation, and the preparation could not be repeated.

(ii) The water digest after filtering from the residual wood was deep yellow and strongly acid, producing smarting on the skin. It turned red on being rendered alkaline. Its volume was 820 c.c. and it required 238 c.c. of  $N/10$ -sodium hydroxide to neutralise it, or 1190 c.c. per cent. It gave a trace of precipitate with lime-water insoluble in acetic, but soluble in hydrochloric acid, pointing to the presence of a little oxalic acid, and a yellow precipitate with lead acetate soluble in excess. It strongly reduced Fehling's solution, and both neutral and ammoniacal silver nitrate solutions on warming, and also potassium permanganate.

(iii) The residual wood (product A) contained 10.7 per cent. of moisture, and weighed 16.78 grams, equivalent to 14.97 grams of dry material. Loss in weight, 25 per cent. The constants are given below.

*Experiment B.*—11.52 Grams were ozonised in a very rapid stream of gas for thirty-six hours with the same precautions to secure even action, as in experiment A. At the end ozone was passing in excess. The contents of the bottle were digested with  $1\frac{1}{2}$  litres of water at  $90^{\circ}$  for some hours, filtered, and washed. The residual wood (product B) was dried at  $98^{\circ}$ , and weighed 6.82 grams

or 39.2 per cent. Loss in weight, 40.8 per cent. The filtrate was distilled to small bulk to remove as far as possible the volatile acids, and one-half of the liquid remaining in the flask was evaporated to dryness and furfuraldehyde was estimated in it.

One-half gave 0.1520 gram of furfuraldehydophloroglucide. Total furfuraldehyde found = 0.1630 gram. This represents 1.42 per cent., calculated on the original wood taken, or 3.4 per cent. on the soluble portion, assuming that this is represented by the difference between the original weight taken and that of the residue left after the ozone and water treatment.

The other half was also evaporated, and a methoxyl estimation gave AgI = 0.068. Total methoxyl found = 0.16 per cent. on the original weight of beech, or 0.4 per cent. on the soluble portion.

#### *Properties of the Residual Wood.*

(i) *The Beech Wood.*—The “constants” of the beech wood used for experiment were determined as follows:

Hygroscopic moisture = 8.2.

Loss on boiling in 1 per cent. NaOH for five minutes 12.2.

0.9832 gave 0.2801 furfuraldehydophloroglucide. Furfuraldehyde = 15.02.

1.876 gave 0.0606 copper. Copper reduced = 3.23.

0.2902 „ 0.1368 AgI.  $\text{OCH}_3$  = 6.2 per cent.

(ii) *Product A.*

Hygroscopic moisture = 10.8.

Loss on boiling in 1 per cent. NaOH = 18.75.

0.0915 gave 0.1631  $\text{CO}_2$  and 0.0518  $\text{H}_2\text{O}$ . C = 48.61; H = 6.29.

1.744 „ 0.2372 furfuraldehydophloroglucide. Furfuraldehyde = 14.68.

(iii) *Product B.*

Loss in 1 per cent. NaOH = 30.63 per cent.

0.1282 gave 0.2736  $\text{CO}_2$  and 0.0679  $\text{H}_2\text{O}$ . C = 46.84; H = 5.87.

1.056 „ 0.2751 furfuraldehydophloroglucide. Furfuraldehyde = 13.75.

1.2035 gave 0.1633 copper. Copper reduced = 13.57 per cent.

These results are collected in the following table, the values previously obtained for jute (*loc. cit.*, p. 509) being included:

TABLE II.

	Original beech.	Product A.		Product B.		Original jute.	Jute, Ozone, 6 hours
		Ozone, 15 hours.	Ozone, 30 hours.	Ozone, 30 hours.	Ozone, 30 hours.		
Residue .....	100.0	74.9	59.2	100.0	67.2		
Loss in weight .....	—	25.1	40.8	—	32.8		
Composition C .....	49.1	48.61	46.84	46.5	47.81		
"    H .....	5.6	6.29	5.87	6.0	6.4		
O, H ratio .....	—	7.1	8.1	8.0	7.8		
Furfuraldehyde* .....	15.0	14.68	13.75	7.8	5.44		
Furfuraldehyde: †							
(a) in fibre .....	—	11.02	8.14	—	3.25		
(b) in solution .....	—	—	1.42	—	1.43		
Total furfuraldehyde .....	15.0	—	9.56	7.8	5.4		
Methoxyl* .....	6.22	—	3.2	—	—		
Copper number .....	8.23	—	13.57	—	—		
Loss 1% NaOH (5 mins.) .....	12.20	18.75	30.63	9.4	18.4		

\* Calculated as yielded by 100 grams of the product.

† Calculated as yielded by 100 grams of original material.

It will be seen that oxidation by ozone in the presence of water for thirty hours and subsequent digestion with water removes 40 per cent. of the wood substance. Part of this is oxidised to carbon dioxide and acetic and formic acids; another part is made soluble in water, and passes into solution in a more or less modified form. The water-soluble part still yields 1.42 per cent. of furfuraldehyde (on 100 grams of beech taken) out of the 15 per cent. given by the original wood. The solid residue yields 8.14 per cent., so that, assuming no development of furfuraldehyde-yielding groups to occur during the oxidation, there is a reduction of the total furfuraldehyde yield from 15 to 9.56, or 5.44 per cent. This may point to a destruction of 36 per cent. of the furfuraldehyde-yielding complex, so that the "balance sheet" of this constituent may be as follows:

	Beech.	Jute.
Remaining in the woody product .....	54	50
Remaining in the soluble portion .....	10	19
"Destroyed" .....	36	31
	100	100

The jute fibre can be regarded as a complex of:

$\alpha$ -Cellulose.	$\beta$ -Cellulose.	Lignone.
65	15	20
(Cross and Bevan, "Researches," I, 135.)		

Of these the  $\beta$ -cellulose yields practically the whole of the furfuraldehyde, some 8 per cent. The fact that treatment with ozone until the lignone reaction disappears results in a loss of 33 per cent. in weight would be accounted for by the assumption

that the whole of the lignone and half the  $\beta$ -cellulose were removed. This would require a loss of 28 per cent., and other experiments showed (T., 1912, 101, 506) that the  $\alpha$ - and  $\beta$ -cellulose are also slightly attacked, making up the additional loss of about 5 per cent.

The beech wood used in these experiments was not boiled with alkali, but only extracted with water and alcohol. It might therefore contain some 5–10 per cent. of "wood gum," a substance giving 30 to 50 per cent. of furfuraldehyde, so that the statistical calculation in this case is not so satisfactory as with jute. The same experiments have shown, however, that ozone attacks the lignified portions of the beech rapidly at first, but later the attack is confined chiefly to the already oxidised lignone, and also partly to the cellulose portion; thus, during the last six hours some of the  $\beta$ -cellulose is either oxidised completely to carbon dioxide or converted to soluble products. With the thirty-hour product *B*, the loss of weight of 40 per cent. is therefore also probably due to the removal of nearly all the lignone, together with some proportion of the  $\beta$ -cellulose. In this respect the action is similar to that taking place in the bisulphite process, in which the lignone is removed largely in combination with the  $\beta$ -cellulose, the loss being some 50 per cent., and differs from the action of chlorine, in which the lignone alone is removed, the loss of weight then amounting to 40 per cent. in the case of beech wood. This would account for the reduction of the furfuraldehyde content from 15 to 8 per cent., and also for the fact that the product *B* does not, as with jute, show the composition of an oxycellulose. The jute fibre lost 33 per cent. of its weight, and gave a product containing 43.8 per cent. of carbon, and yielding 5.7 per cent. of furfuraldehyde, agreeing in composition and properties with an oxycellulose of high furfuraldehyde content. That this was the  $\alpha$ - and  $\beta$ -cellulose of the jute was shown by the observation that on chlorination no lignone reactions were observed, and practically no further loss of weight took place (*loc. cit.*, p. 507). In the case of beech, however, with a loss of weight of 40 per cent. the product still contains 46.6 per cent. of carbon, and yields 13.7 per cent. of furfuraldehyde. It has an oxygen hydrogen ratio of 8:1, and in composition is thus very similar to jute itself. It has acquired oxycellulose characters, notably a copper number of 13.6 compared with 3.2, and its solubility in dilute sodium hydroxide has become 30.6 instead of 12.2 per cent.

The methoxyl content of product *B* is also very significant. The values obtained were confirmed by duplicate experiments, and show that whereas the beech yielded 6.2 per cent. of methoxyl, product *B*

only yielded 3.2 per cent., or 1.92 per cent., calculated on the original weight of the beech. At the same time, only 0.16 per cent. was found in the soluble portion, so that the percentage distribution of this constituent would be: in the solid portion, 31; in solution, 2.6; destroyed, 66.4 per cent. These figures indicate an oxidation of 66 per cent. of the groups containing methoxyl. These are known to be situated largely in the lignone complex, but also to a lesser extent in the  $\beta$ -cellulose portion of the lignocellulose. Cross and Bevan, for example, found (*Ber.*, 1893, 26, 2520) that with an original jute containing 4.5 per cent. of methoxyl the  $\alpha$ - and  $\beta$ -cellulose isolated from it contained 1.2 per cent. These values indicate that 84 per cent. of the methoxyl groupings are present in the lignone and 16 per cent. in the cellulose. In beech product B 31 per cent. is present.

These results all point to the conclusion that product B, the residue from a prolonged treatment with ozone, consists of the  $\alpha$ -cellulose, part of the  $\beta$ -cellulose, and (unlike the jute product) of a proportion of some lignified constituent. The latter can be accounted for by the fact that apart from the "wood gum," the lignified portions of the woods of long growth are more complex than those of the annual fibre jute.

The product A, fifteen hours treatment, shows intermediate characters, the loss of weight being 25 per cent. and the furfuraldehyde in the solid substance being 11 instead of 15 per cent. Its composition (C-48.6: H-6.3) differs only slightly from that of the original beech, and indicates the gradual oxidation of the lignone portion.

#### *The Nature of the Action of Ozone on Lignocellulose.*

The experimental work on jute and beech has resulted in the following observations of which an explanation must be sought.

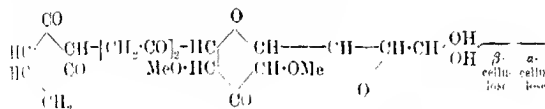
- (1) Ozone has practically no action on the dry substance. In anhydrous media the action is one of slow oxidation.
- (2) In the presence of water there is a rapid initial development of acid products, followed by a fall in the production to one-tenth of the former value in the case of beech.
- (3) Carbon dioxide is produced throughout, the decrease in the rate of production after six hours being small.
- (4) Volatile acids, namely, 2.6 per cent. (beech) and 2.5, 5.3, and 3.5 per cent. (jute), calculated as acetic acid, are obtained on distillation in steam. These consist of acetic and formic and another acid of reducing character (beech). With jute the proportion of formic acid is 30-50 per cent. of the total volatile acid.

(5) The non-volatile acid liquid has three to five times the acid value of the volatile acids. It contains reducing substances of an aldehydic or ketonic character. Oxalic acid is present only in minute quantity; phenols are absent.

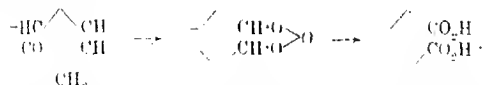
(6) Some 40 per cent. of the wood is oxidised or rendered soluble in water.

(7) The solid product has a high furfuraldehyde content, but contains only a small proportion of methoxyl.

The schematic formula which embodies the known reactions of lignocellulose given by Cross and Bevan ("Researches," III., p. 104) formulates the lignone group as (a) a keto-R-hexene group joined by  $\text{CH}_2\text{CO}$  residues to (b) a pyrone ring containing two methoxyl groups, this ring being connected through a chain of carbon atoms to the  $\beta$ - and  $\alpha$ -cellulose, thus:



The ozone molecule attaches itself, in the absence of water, to unsaturated linkings forming ozonides; in the presence of water these ozonides are decomposed at the moment of formation, yielding aldehydes or acids. With the *cyclohexenone* group (a) the result would probably be:

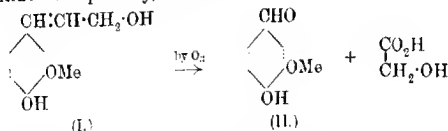


This would account for the rapid initial development of acidic substances, the ozone being entirely absorbed at the unsaturated linking. At the same time, the opening up of the ring at this point determines (as with chlorine) the removal of the whole of the lignone from the cellulose complex. In this case the  $\beta$ -cellulose is partly removed, also in combination with the lignone, as in the bisulphite process. Further oxidation of these groupings at once begins. The formation of acetic acid indicates the rupture of the attachment between the *cyclohexenone* and the pyrone groups. The former group probably gives acids of a ketonic character accounting for the powerful reducing properties of the water digest. The pyrone grouping in its oxygen atom and carbonyl group presents to ozone two points of attack. Unstable peroxides will probably be formed, the decomposition of which will further the process of oxidation. The fact that only 30 per cent. of the methoxyl constituent is found in the wood residue points to the almost complete

destruction of this grouping, and by the cleavage of such a pyrone ring formic acid could easily be produced.

The results, so far as they carry, therefore, are fully in agreement with the formulation of the lignocellulose complex proposed by Cross and Bevan. On the other hand, they do not lend support to the alternative view of Klason (*Beiträge zur Kenntniss der chemischen Zusammensetzung des Fichtenholzes*, Berlin, 1911), that the "lignin" (of coniferous woods) is largely of an aromatic nature, being based on coniferyl alcohol (I) and of a condensed anhydride of hydroxyconiferyl alcohol or allied compound.

If this were the case, the action of ozone should yield vanillin (II) in considerable quantity, thus:



In none of the products obtained, however, could this aldehyde be detected. It might be urged that if formed it would be at once oxidised by ozone to simpler derivatives. Aldehydes, however, are remarkably stable towards ozone, and vanillin is at the present time largely manufactured by the oxidation of *isoeugenol* by ozone, according to the observation first made by Otto (*Ann. Chim. Phys.*, 1898, [vii], 13, 77). It is true that vanillin has been obtained from woods by various processes of hydrolysis and oxidation (Singer, *Monatsh.*, 1882, 3, 409; Grafe, *ibid.*, 1904, 25, 1004; Czapek, *Zeitsch. physiol. Chem.*, 1899, 27, 141), but only in minute quantity (40 grams from 50 kilos. by Czapek and Grafe). The quantity, if any, produced by ozone must be of a similar order, and this seems to preclude the possibility of any considerable portion of the lignone complex having the coniferyl alcohol basis. Klason further states that the lignin (of coniferous woods) does not yield any acetic acid on oxidation. There is no reason to suppose that the lignin of pine-wood differs essentially from that of beech and jute, yet with both of these a considerable production of acetic acid can be observed as the result of an hour's exposure to dilute ozone. This must surely proceed from the oxidation of the reactive lignone groupings.

Experiments are now in progress which will, it is hoped, throw further light on these problems.

CHEMISTRY DEPARTMENT,  
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LXXVII.—*Experiments on the Walden Inversion.\**  
 Part IX. *The Interconversion of the Optically Active Phenylmethylcarbinols.*

By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

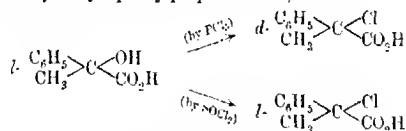
PREVIOUS researches on the Walden inversion have been confined to transformations undergone by carboxylic acids or by their more closely allied derivatives, such as esters. Although the picture of the Walden inversion may not now be very materially altered by an extension of the experimental inquiry to other types, it is nevertheless desirable that such an extension should be prosecuted in order to provide further data for the discussion of the problem on the theoretical side. On this account a study has been made of the phenylmethylcarbinols, and the enantiomorphously related isomerides have been converted one into the other.

Thanks to the work of Pickard, Kenyon, and others, it is now possible to obtain a whole series of optically active alcohols by the resolution of the *dl*-forms. The phenylmethylcarbinols (I) were

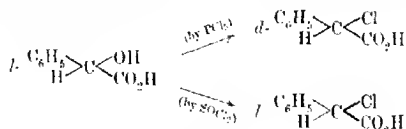


selected for the present purpose in order to contrast their behaviour with that of the  $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acids (II), which had already been studied. Moreover, the presence of a phenyl group in other compounds causes group displacement to be accompanied by racemisation to a degree which is generally considerable. It was therefore of some interest to find out if a similar effect would be observed in the case of the phenylmethylcarbinols.

Phosphorus pentachloride and thionyl chloride behave differently towards *l*- $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid, thus:



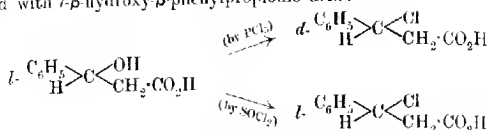
A similar difference in behaviour was observed in other instances, thus, with *l*-mandelic acid:



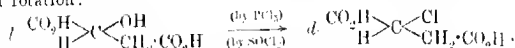
\* Previous papers: T., 1908, **93**, 811; 1909, **95**, 777; 1910, **97**, 121, 1016, 1355, 2594; 1911, **99**, 1910; 1912, **101**, 390.



and with *l*-β-hydroxy-β-phenylpropionic acid:



With malic acid, however, both reagents cause a change of sign of rotation:



Now, Pickard and Kenyon (T., 1911, **99**, 45) have prepared a number of haloids from the active alcohols by the action of halogen hydride, and in every case the formation of haloid was accompanied by a change of sign of rotation. Attempts to reconvert these haloids into the optically pure alcohols were unsuccessful; the values recorded for the haloids are undoubtedly too low, and the authors state that "the preparation of them with any degree of certainty that racemisation has been avoided is tedious." The action of hydrogen chloride at 0° on *d*-phenylmethylecarbinol led to the formation of a levorotatory α-chloroethylbenzene with  $[\alpha]_D^{25} -5.8^\circ$ . Pickard and Kenyon point out, however, in a recent communication (Ber., 1912, **45**, 1592) that *sec*-*d*-octyl alcohol is converted by hydrogen bromide into *sec*-*l*-octyl bromide, from which the original alcohol can be regenerated by means of silver oxide and water.

We find that phosphorus trichloride behaves like hydrogen chloride towards *d*-phenylmethylecarbinol; a change of sign of rotation occurs, the haloid having the value  $[\alpha]_D^{25} -8.1^\circ$ . On the other hand, when thionyl chloride is employed, the sign of rotation is unchanged, and the resulting α-chloroethylbenzene has  $[\alpha]_D^{25} +50.6^\circ$ . This is a very striking example of the fact that when the hydroxy-group in an optically active compound is displaced by the chlorine atom by the agency of thionyl chloride, the extent of the racemisation is much less than when the displacement is effected by other agents.

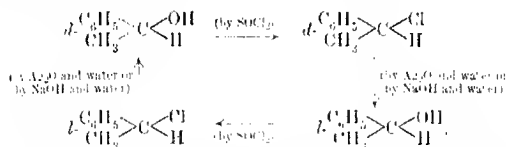
The action of acetyl chloride on the active phenylmethylecarbinols leads to the formation of α-chloroethylbenzene, the product having the same sign of rotation as the alcohol used as the starting point. We attach little importance to this observation, however, since the product may not be quite free from ester (see experimental part).

The displacement of chlorine in the active α-chloroethylbenzenes, formed by the interaction of thionyl chloride and the alcohols, was first of all effected by silver oxide and water. A change of sign of rotation occurred, the alcohol isolated from *d*-α-chloroethyl-

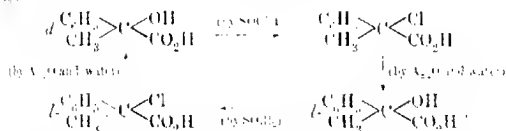
benzene, for example, having  $[\alpha]_D -13.2^\circ$ . Since the original *d*-phenylmethylcarbinol had  $[\alpha]_D +43.4^\circ$ , it will thus be seen that a considerable amount of racemisation had occurred during the displacement reactions. The extent of the racemisation is much more pronounced when the displacement of the chlorine is effected by aqueous sodium hydroxide. Here again a change of sign of rotation occurs, the resulting alcohol having only  $[\alpha]_D$  about  $-1.7^\circ$ .

The displacement of chlorine by the hydroxy-group is attended by more racemisation in other cases also where aqueous sodium hydroxide is used in place of silver oxide and water. For example, the  $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid, obtained from *l*- $\alpha$ -chloro- $\alpha$ -phenylpropionic acid by means of silver oxide and water, has  $[\alpha]_D +9.4^\circ$  in ethyl-alcoholic solution,\* whereas racemisation is complete when aqueous sodium hydroxide is used (T., 1910, 97, 1016).

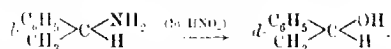
The interconversion of the phenylmethylcarbinols can thus be brought about by the following cycle, which represents the first instance of the interconversion of enantiomorphously related alcohols by the Walden inversion:



It is interesting to note the close parallelism of these changes with the following undergone by the  $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acids:



Reference may be made here to certain racemisation phenomena already recorded in the literature regarding the phenylmethylcarbinols. Marekwald and Meth (*Ber.*, 1905, 38, 801) investigated the change:



and drew the conclusion, from the small rotatory power of the resulting alcohol, namely,  $[\alpha]_D +2.7^\circ$ , that partial racemisation had taken place. The same action was studied by Holmberg (*Ber.*, 1912,

\* *d*- $\alpha$ -Hydroxy- $\alpha$ -phenylpropionic acid has  $[\alpha]_D +37.7^\circ$ .

45, 997), who, being unacquainted with the work of Pickard and Kenyon (T., 1911, 99, 45; compare also *Ber.*, 1912, 45, 1592), was in error in supposing that he had obtained the optically pure alcohol. The following observations are recorded by Holmberg:

(1) Total racemisation occurred when a dextrorotatory phenyl methylcarbinol with  $\alpha_D^{25}$  ( $[\alpha]_D^{25}$ )  $+5.0^\circ$  was acted on by hydrogen bromide.

(2) A change of sign of rotation occurred when a levorotatory phenylmethylcarbinol with  $\alpha_D^{25}$  ( $[\alpha]_D^{25}$ )  $-4.40^\circ$  was acted on by phosphorus pentabromide.

(3) A change of sign of rotation occurred when a dextrorotatory  $\alpha$ -bromoethylbenzene with  $\alpha_D^{25}$  ( $[\alpha]_D^{25}$ )  $+1.37^\circ$  was acted on by silver oxide and water.

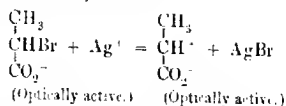
We also investigated the action of thionyl chloride on *d*-amyl alcohol, the levorotatory constituent of fusel oil. Le Bel had shown many years ago that a change of sign of rotation occurred when this alcohol interacted with phosphorus pentachloride, and subsequent work has shown that derivatives of *d*-amyl alcohol are dextrorotatory. The amyl chloride obtained by means of thionyl chloride is also dextrorotatory; *d*-amyl chlorosulphinate was formed as an intermediate product, from which sulphur dioxide was readily eliminated by heating under the ordinary pressure. Thus the amyl chloride, obtained by the action either of phosphorus pentachloride or of thionyl chloride on the alcohol, is dextrorotatory, a result which was expected, since the hydroxy-group of the alcohol is not directly attached to the asymmetric carbon atom.

A contribution to the theoretical side of the problem of the Walden inversion has recently been published by Biilmann (*Annalen*, 1912, 388, 330), who criticises adversely certain conceptions which had been previously advanced by E. Fischer (*ibid.*, 1911, 381, 123; 386, 374). To this criticism Fischer has replied (*ibid.*, 1912, 394, 350). In addition to the points dealt with by Fischer, there are several aspects submitted by Biilmann with which we find ourselves unsympathetic, and we accordingly take the present opportunity of referring to these.

In the first place, the displacement of halogen by the hydroxy-group by the aid of silver oxide and water is discussed, the formation of lactic acid from optically active  $\alpha$ -bromopropionic acid being cited as a typical example. The suggestion is made that in such displacements the action is really one between water and silver salt, and, according to Biilmann, experimenters on the Walden inversion have failed to realise this. Biilmann has neglected to observe, however, that we have actually studied the action of water on silver salt in several instances; for example, it was pointed out

(T., 1908, 93, 811) that silver *l*-phenylchloroacetate was prepared by the addition of silver nitrate to sodium *l*-phenylchloroacetate, and the sparingly soluble precipitate was separated. The action of water on it at the ordinary temperature was then examined, and contrasted with the action of water and silver carbonate on *l*-phenylchloroacetic acid; these two actions were similar in so far as a dextrorotatory mandelic acid was isolated in each case.\* Moreover, in subsequent work we invariably recognised that the action of silver oxide (or silver carbonate) and water on a halogen substituted acid could anyhow be attended by the action of water on the silver salt.† There is little doubt, however, that in certain cases where silver oxide and water have been employed for the purpose of displacing halogen, the action is not simply one of water on silver salt, but is more complex. For instance, when *l*- $\alpha$ -chloro- $\alpha$ -phenylpropionic acid,  $\begin{smallmatrix} \text{C}_6\text{H}_5 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{C} \begin{smallmatrix} \text{Cl} \\ | \\ \text{CO}_2\text{H} \end{smallmatrix}$ , is shaken with water at the ordinary temperature, the chlorine is displaced with remarkable celerity, and the solution becomes optically inactive owing to the production of *r*- $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid,  $\begin{smallmatrix} \text{C}_6\text{H}_5 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{C} \begin{smallmatrix} \text{OH} \\ | \\ \text{CO}_2\text{H} \end{smallmatrix}$  on the other hand, with silver oxide and water, a dextrorotatory  $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid is formed from the *l*-chloro-acid (T., 1910, 97, 1016). It is quite likely that two distinct actions are here proceeding concomitantly. Nevertheless, the possibility that the mechanism of the action of water on the chloro-acid is identical with that of the action of water on the silver salt of the chloro-acid must be admitted in some cases, and the kinetic studies of Senter and of Holmberg may be expected to throw much light on a problem of this nature.

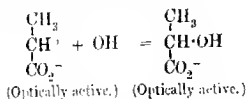
According to Biilmann, no Walden inversion takes place when the halogen in an  $\alpha$ -halogen acid is displaced by the hydroxy-group by means of silver oxide and water. The action is regarded as one of direct substitution, the silver salt being dissociated in aqueous solution, and the positive silver ion withdrawing the bromine to form undissociated haloid, thus:



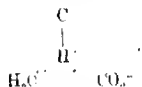
\* Compare also the action of water on lead, ferric and mercurous *l*-phenylchloroacetates (T., 1909, 95, 777), on silver *d*- $\alpha$ -bromo- $\beta$ -phenylpropionate (T., 1910, 97, 1009), and on silver *l*-dibromosuccinate (T., 1912, 101, 1196).

† In practice, it is, as a rule, more convenient to conduct the displacement of halogen by means of silver oxide and water rather than to separate the silver salt and then act on it with water.

Then the "Zwitterion" combines with the negative hydroxy-ion of water to form an ion of lactic acid:

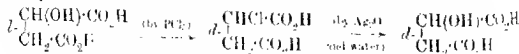


Now, on the above representation the central carbon atom which was originally quadrivalent apparently ceases to have a tetrahedral environment, and, since a "Zwitterion" is supposed to be electrically neutral, it cannot even be urged that a free electric charge plays the part of the fourth grouping which is necessary for the retention of asymmetry. In order therefore to visualise a "Zwitterion" like that postulated above, which will preserve an enantiomorphous configuration after it has been formed from the active bromopropionic ion, it becomes necessary to imagine a grouping of this kind:



The carbon atom is here represented at the apex of a tetrahedron, and the three other groups at the corners. Surely, however, optical activity must vanish before a complex of this type can possess the free existence in solution, such as is tacitly implied by Billmann for the "Zwitterion." Otherwise, the formation of an optically active structure containing an asymmetric tervalent carbon atom must be admitted, a view for which there is not the slightest experimental evidence. On these grounds, Billmann's conception, however suggestive it may be, can hardly be accepted as tenable.

At least two separate displacement reactions are necessary for the proof of the occurrence of a Walden inversion; thus, with the interconversion of the phenylmethylecarbinols, we have (1) the displacement of the hydroxy-group by means of thionyl chloride, and (2) the elimination of chlorine in the resulting  $\alpha$ -chloroethylbenzene. A configurational change occurs at one of these stages, but at which one it is at present impossible to assert with definiteness. It is, of course, true that in the earlier experimental work on the subject it was customary to regard as "normal" one of the displacement reactions involved, and the other as "abnormal." For example, in the changes examined by Walden:



the action of phosphorus pentachloride was designated as "normal,"

that is, unaccompanied by configurational change, whereas the action of water and silver oxide was called "abnormal." When, however, the experimental data of the past few years are carefully reviewed, it must be conceded that, in practically every case, it is impossible to fix a Walden inversion as occurring definitely during any single displacement reaction (compare Fischer, *loc. cit.*). This is not, however, the conclusion which is arrived at by Büllmann, who submits the following generalisations:

(1) The action of water on optically active silver salt is one of direct displacement, "Stellvertretung" (or, to use the old term, is "normal"), since it occurs between the cation and halogen.

(2) The action of nitrous acid on active amino-acids is one of direct displacement.

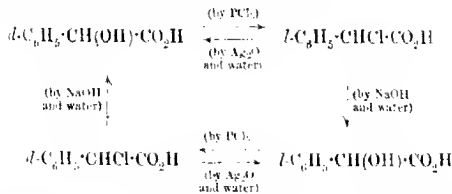
(3) The action of phosphorus pentachloride on active hydroxy-acids involves a configurational change.

(4) The action of sodium hydroxide or of ammonia on an active halogen acid involves a configurational change.

These ideas are unfortunate, as they are not in accordance with the facts.

Büllmann (*loc. cit.*, p. 335) writes as follows: "Vorausgeschickt sei die Bemerkung, dass das experimentelle Material, welches besonders E. Fischer und Walden in den letzten 14 Jahren gebracht haben, so vorzüglich es auch in anderer Hinsicht sein mag, doch so wenig einheitlich ist, dass eine exakte Behandlung der Frage ohne Zweifel eine Neubearbeitung fordern wird. Selbst in den drei Gruppen, wo das Material am wenigsten Lücken zeigt, der Alanin-Gruppe, der Asparaginsäure und der Valin-Gruppe, gilt dieser Einwand gegen die Einheitlichkeit." There is, however, a fourth group, namely, the mandelic acid group, which has been investigated with some degree of completeness in this laboratory. Had Büllmann been cognisant of the work in this branch, he would doubtless have recognised that the above-mentioned views cannot be entertained. In this connexion it will suffice to refer to two methods by which the active mandelic acids can be interconverted.

The following transformations can be effected:



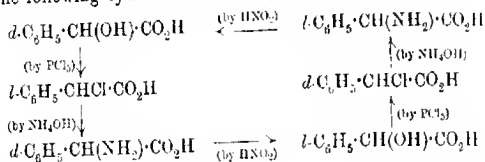
If the first of Büllmann's theses be accepted, then the *L*-chloro-acid

VOL. CIII.

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passes into *d*-mandelic acid without configurational change; but then the action of phosphorus pentachloride on *d*-mandelic acid ought, according to Biilmann, to give *d*-chloro-acid, which it does not. If therefore Biilmann's first thesis (regarding the action of water on silver salt) is correct, his third thesis (regarding the action of phosphorus pentachloride) is incorrect, and vice versa. Also, if, in the above cycle, Biilmann's third thesis is accepted, then his fourth thesis (regarding the action of sodium hydroxide) is invalid, and vice versa.

The following cycle can also be experimentally realised:



It will be seen that these results are also in disagreement with Biilmann's views.

#### EXPERIMENTAL.

##### *Action of Thionyl Chloride on the Active Phenylmethylcarbinols.*

*d*-Phenylmethylcarbinol was prepared by the resolution of the hydrogen succinic *dl*-ester by means of brucine (Pickard and Kenyon, T., 1911, 99, 45). It boiled at  $104^\circ/23$  mm., and had  $[\alpha]_D^{20} + 43.4^\circ$ , values in satisfactory agreement with those quoted by Pickard and Kenyon.

When the *d*-alcohol (4 grams) was added gradually to thionyl chloride (10 grams), there was no pronounced rise of temperature, although the action was vigorous after each addition. After fifteen minutes at the ordinary temperature, the liquid was distilled under diminished pressure. Yield, 4 grams.

*d*- $\alpha$ -Chloroethylbenzene,  $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CH}_3$ , is an oil which boils at  $85^\circ/20$  mm.

Found, Cl = 25.3 (by Stepanow's method). Calc., Cl = 25.2 per cent.

It had  $\alpha_D^{20} + 26.90^\circ$  in a 50 mm. tube;  $d_4^{20}$  1.0631; whence  $[\alpha]_D^{20} + 50.6^\circ$ .

Although it was anticipated, in the light of previous experience in displacement reactions, that some racemisation would accompany the substitution of the hydroxy-group in *d*-phenylmethylcarbinol by a chlorine atom, there is no proof that any such phenomenon had occurred in the present instance. On the contrary, it is permissible to draw the conclusion that the above-mentioned chloro-substitution product can contain only very little of the *dl*-form. In the event

of racemisation accompanying the displacement, it is extremely probable that the chloroethylbenzene, obtained from different preparations by the agency of thionyl chloride, would not always possess the same rotatory power. It was found, however, in a second experiment, where 5 grams of the *d*-alcohol and 15 grams of thionyl chloride were employed, that the resulting chloroethylbenzene had  $\alpha_D + 26.85^\circ$  in a 50 mm. tube.

The *l*-alcohol was not prepared in the pure state, but a product with a fairly high rotation was obtained from the mother liquors resulting from the crystallisation of the brucine salt of the hydrogen mecinic *d*-ester. Forty-one grams of this product, which had  $\alpha_D - 26.70^\circ$  in a 1-dm. tube, were added as before to 56 grams of thionyl chloride. The resulting  $\alpha$ -chloroethylbenzene boiled at  $33.7/20$  mm., and had  $\alpha_D^{20} - 32.05^\circ$  ( $l=1$ ),  $d_4^{20}$  1.0632; whence  $[\alpha]_D^{20} - 30.1^\circ$ . (Found, Cl=25.3. Calc., Cl=25.2 per cent.) In a similar manner, the chloroethylbenzene, prepared from a levorotatory alcohol with  $\alpha_D - 29.0^\circ$  ( $l=1$ ), had  $\alpha_D - 33.20^\circ$  ( $l=1$ ).

*Action of Phosphorus Trichloride on the Active Phenylmethylcarbinols.*

Phosphorus trichloride (20 grams) was cooled to  $0^\circ$ , and the *l*-alcohol (5 grams) was added drop by drop. The product was fractionated, and the portion boiling at  $80-80.5/15$  mm. was collected, and found to be levorotatory with  $\alpha_D^{20} - 4.32^\circ$  ( $l=0.5$ ),  $[\alpha]_D^{20} - 8.638$ ; whence  $[\alpha]_D^{20} - 8.1^\circ$ . Found, Cl=25.1. Calc., Cl=25.2 per cent.

This change of sign of rotation was confirmed by the action of phosphorus trichloride (20 grams) on a levorotatory phenylmethylcarbinol (5 grams), having  $\alpha_D - 32.0^\circ$  ( $l=1$ ). The chloroethylbenzene amounted to 3 grams, and had  $\alpha_D + 2.95^\circ$  ( $l=0.5$ ). Found, Cl=25.1. Calc., Cl=25.2 per cent.

The action of phosphorus pentachloride on the alcohols led to the formation of viscid oils containing phosphorus, and was not therefore thoroughly investigated.

*Action of Acetyl Chloride on the Active Phenylmethylcarbinols.*

The behaviour of acetyl chloride towards *d*-phenylmethylcarbinol was studied in consequence of an observation made by Radziszewski (*Ber.*, 1874, 7, 140), who added the optically inactive alcohol to an excess of acetyl chloride and found that, when the product, which consisted mainly of acetic acid and  $\alpha$ -chloroethylbenzene, was treated with silver acetate, it gave the ester derived from phenylmethylcarbinol.  $\alpha$ -Chloroethylbenzene was not, however, isolated by Radziszewski in the course of his examination of this action.



Five grams of *d*-phenylmethylcarbinol were added drop by drop during fifteen minutes to 20 grams of acetyl chloride, the liquid being kept cold. After thirty minutes at the ordinary temperature, the oil was distilled. The fraction boiling at 80–81°/15 mm. amounted to 3.7 grams, and was dextrorotatory, having  $\alpha_D +0.95^\circ$  in a 50 mm. tube. This liquid was warmed at 40° for ten minutes with 5 grams of acetyl chloride, and again distilled. The activity of the fraction boiling at 80–80.5°/15 mm. was practically the same as before, the value obtained being  $\alpha_D +0.90^\circ$  in a 50 mm. tube. It is possible, however, that a trace of ester may have been present even after this treatment. The value for the density, namely,  $d_4^{20}$  1.061, is rather low, and the analysis was not very satisfactory. Found, Cl=24.7. Calc., 25.2 per cent.

A similar result was arrived at when the levorotatory alcohol was examined from the same standpoint. Ten grams of an alcohol with  $\alpha_D -20.6^\circ$  ( $l=1$ ) were added to 20 grams of acetyl chloride during half an hour. After fractionation, 6 grams of an oil boiling at 85°/20 mm. were collected, having  $d_4^{20}$  1.059. On polarimetric examination, the product was found to be levorotatory, giving  $\alpha_D -0.73^\circ$  in a 50 mm. tube. Found, Cl=24.8. Calc., Cl=25.2 per cent.

*Action of Silver Oxide and Water on the Active  $\alpha$ -Chloroethylbenzenes.*

Six grams of the partly racemised  $\alpha$ -chloroethylbenzene with  $[\alpha]_D^{20} -30.1^\circ$  were added to 60 c.c. of water, and the mixture shaken with silver oxide (6 grams) for two hours, and then heated on the water-bath for fifteen minutes. The alcohol was separated by distillation in steam, extracted with ether, and fractionated under ordinary pressure. The portion boiling at 196° to 200° (2 grams) had  $\alpha_D^{20} +3.71^\circ$  ( $l=0.5$ ),  $d_4^{20}$  1.0135; whence  $[\alpha]_D^{20} +7.3^\circ$ . Found, C=78.0; H=8.5. Calc., C=78.6; H=8.3 per cent.

A change of sign of rotation had thus been effected by the displacement of the chlorine atom in *l*- $\alpha$ -chloroethylbenzene by the hydroxy-group, and it was also obvious that a considerable amount of racemisation had occurred.

The resulting alcohol with  $[\alpha]_D +7.3^\circ$  was added to an equal weight of phenylcarbinide, and warmed gently. After twenty-four hours, the crystals of the phenylurethane were removed and washed with light petroleum. Their solution in benzene was dextrorotatory:

$l=2$ ;  $c=5.015$ ;  $\alpha_D$  1.61°;  $[\alpha]_D$  16.1°.  
(Found, C=74.2; H=6.3. Calc., C=74.6; H=6.3 per cent.)

When this product was crystallised from light petroleum, the optically active phenylurethane tended to accumulate in the filtrate; thus, after one crystallisation, the crystals had  $[\alpha]_D +6.1^\circ$  in benzene solution, and after a further crystallisation, the activity had diminished to  $[\alpha]_D +1.3^\circ$ . The melting point at this stage was  $91-93^\circ$ , whereas the phenylurethane of *dl*-phenylmethylcarbinol melts at  $94^\circ$  according to Klages and Allendorff (*Ber.*, 1898, **31**, 1004).

The phenylurethane of *d*-phenylmethylcarbinol was prepared from the pure alcohol, and crystallised from light petroleum, from which it separates in glassy needles, m. p.  $92^\circ$ :

0.2036 gave 0.5535  $\text{CO}_2$  and 0.115  $\text{H}_2\text{O}$ .  $\text{C}=74.1$ ;  $\text{H}=6.3$ .

$\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}$  requires  $\text{C}=74.6$ ;  $\text{H}=6.3$  per cent.

A determination of its specific rotation was made in benzene solution:

$$l=2; c=4.864; a_D^{20}+9.87^\circ; [\alpha]_D^{20}+101.5^\circ.$$

It is accordingly possible to prepare a mixture of the *r*- and *d*-phenylurethanes from *l*-phenylmethylcarbinol, but, unless the *d*-phenylurethane preponderated in the mixture, its isolation by crystallisation could not readily be effected.

Nine grams of *d*- $\alpha$ -chloroethylbenzene with  $a_D^{20}+26.85^\circ$  ( $l=0.5$ ), prepared from *d*-phenylmethylcarbinol, were added to 90 c.c. of water, and the mixture shaken on the machine for two hours with the silver oxide prepared by the action of baryta on 17 grams of silver nitrate. The alcohol was isolated by steam distillation, etc. The fraction boiling at  $198-201^\circ$  amounted to 4.4 grams. (Found,  $\text{C}=78.4$ ;  $\text{H}=8.4$ . Calc.,  $\text{C}=78.6$ ;  $\text{H}=8.3$  per cent.) The alcohol consisted of a mixture of *l*- and *dl*-phenylmethylcarbinols. The following observations were made:

$$l=1; a_D^{20}-13.32^\circ; a_4^{20}1.0118; [\alpha]_D^{20}-13.2.$$

Two grams were converted into the phenylurethane, and the resulting solid crystallised from light petroleum, and then examined polarimetrically in benzene solution:

$$l=2; c=7.2; a_D^{20}-3.22^\circ; [\alpha]_D^{20}-22.4^\circ.$$

After an additional crystallisation from light petroleum, the mixture contained a less proportion of the active phenylurethane than before, the specific rotatory power being  $-17.6^\circ$  for  $c=7.12$ . An analysis was made of the less active mixture. (Found,  $\text{C}=74.7$ ;  $\text{H}=6.3$ . Calc.,  $\text{C}=74.6$ ;  $\text{H}=6.3$  per cent.)

*Action of Sodium Hydroxide and Water on the Active  
α-Chloroethylbenzenes.*

Six grams of the partly racemised α-chloroethylbenzene with  $[\alpha]_D^{20} - 30.1^\circ$  were boiled for two hours with a solution of 6 grams of sodium hydroxide in 60 c.c. of water. The alcohol was obtained as usual. The fraction boiling at  $196-200^\circ$  (2 grams) was dextro rotatory, having  $\alpha_D + 0.65^\circ$  ( $l = 0.5$ ).

(Found, C = 77.8; H = 8.3. Calc., C = 78.6; H = 8.3 per cent.)

The mixture of the *d*- and *r*-phenylurethanes was made as before. The crude product had  $[\alpha]_D + 0.95^\circ$  in benzene solution, and became quite inactive after one crystallisation.

Nine grams of *d*-α-chloroethylbenzene were boiled for three hours with a solution of 9 grams of sodium hydroxide in 90 c.c. of water. The yield of alcohol boiling at  $197-200^\circ$  amounted to 2.5 grams. The liquid was laevorotatory, giving  $\alpha_D - 0.85^\circ$  ( $l = 0.5$ ). The phenylurethane prepared from it had  $[\alpha]_D - 1.15^\circ$  in benzene solution, and, after one crystallisation from light petroleum, it was inactive. (Found, C = 74.8; H = 6.3. Calc., C = 74.6; H = 6.3 per cent.)

The displacement of chlorine by the hydroxy-group was also effected in the following manner. Ten grams of the laevorotatory α-chloroethylbenzene with  $[\alpha]_D^{20} - 30.1^\circ$  were dissolved in 30 c.c. of glacial acetic acid, and shaken for an hour with 15 grams of silver acetate. The mixture was finally heated on the water-bath. The silver chloride was removed, and the acetic acid distilled off under diminished pressure, and then the acetate was distilled. The acetate was saponified, the resulting alcohol was distilled in a current of steam, and isolated in the customary manner. Five grams were obtained with b. p.  $196-197^\circ$  and  $\alpha_D + 1.60^\circ$  in a 50 mm. tube.

*Action of Thionyl Chloride on d-Amyl Alcohol.*

The method of Marckwald and McKenzie (*Ber.*, 1901, **34**, 454) was employed for the preparation of *d*-amyl alcohol. The product contained, however, a little of the isomeric *iso*-amyl alcohol, since its specific rotatory power was  $-5.7^\circ$ , whereas the pure alcohol has  $[\alpha]_D - 5.9^\circ$ . Twelve grams were gradually added to 30 grams of thionyl chloride, and, after one hour, the liquid was distilled under diminished pressure. The yield of the chlorosulphinate was 22 grams.

*d*-Amyl chlorosulphinate,  $C_5H_{11}O\cdot SOCl_2$ , is a colourless oil with a pungent odour, and boils at  $73^\circ/15$  mm. It fumes slightly when exposed to air, and is readily decomposed by water:

Found,  $\text{SO}_2=37.3$ ;  $\text{Cl}=20.7$ .

$\text{C}_5\text{H}_{11}\text{O}_2\text{ClS}$  requires  $\text{SO}_2=37.6$ ;  $\text{Cl}=20.8$  per cent.

It had  $\alpha_D^{14.5} +4.87^\circ$  ( $l=1$ );  $d_4^{14.5} 1.1399$ ; whence  $[\alpha]_D^{14.5} +4.3^\circ$ .

In a second preparation, a compound with the same rotatory power as the preceding was obtained. The rotatory power is not diminished when the sulphinate is redistilled under diminished pressure.

*d*-Amyl chlorosulphinate (22 grams) was heated at  $120^\circ$  for two hours under the ordinary pressure. Sulphur dioxide was evolved. The residue was distilled, and the product, boiling at  $98-99^\circ$ , collected. Yield, 12 grams.

*d*-Amyl chloride is a colourless liquid, boiling at  $98-99^\circ$ . It has  $\alpha_D^{14} +0.75^\circ$  ( $l=0.5$ );  $d_4^{14} 0.8868$ ; whence  $[\alpha]_D^{14} +1.7^\circ$ .

In another preparation the value  $\alpha_D^{14} +2.93^\circ$  in a 2-dcm. tube was obtained; these values agree. The rotation was not altered by redistillation:

0.1488 gave 0.1995 AgCl.  $\text{Cl}=33.2$ .

$\text{C}_5\text{H}_{11}\text{Cl}$  requires  $\text{Cl}=33.3$  per cent.

The value quoted by Le Bel (*Bull. Soc. chim.*, 1876, [ii], 25, 345) for *d*-amyl chloride is  $[\alpha]_D +1.24^\circ$ . The haloid was prepared by Le Bel by the interaction of phosphorus pentachloride and a highly active amyl alcohol, but the preparation appears to have been attended with some racemisation.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

BIRMINGHAM COLLEGE,  
LONDON, E.C.

# ANNUAL GENERAL MEETING,

MARCH 14TH 1913.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,  
in the Chair.

Mr. C. H. HAMPSHIRE and Mr. T. R. MERTON were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society from January, 1912, to date, and a statement was made by the TREASURER as to the Income and Expenditure for 1912. The adoption of the Report of the Council, together with the Balance Sheet and Statement of Accounts for the year ended December 31st, 1912, was proposed by Mr. T. FAIRLEY, seconded by Professor A. G. GREEN, and carried unanimously.

A Vote of Thanks to the Auditors was proposed by the TREASURER, seconded by Dr. S. B. SCHRYVER, and acknowledged by Professor J. M. THOMSON.

## REPORT OF COUNCIL, 1912-1913.

THE Annual Reports of the Council have, in the past, dealt with the work of the Society during the previous calendar year, but the general portion of the present Report refers to the period from the commencement of 1912 to March, 1913, and this portion of future Reports will concern the period from one Annual General Meeting to the next Annual General Meeting.

On the 31st December, 1911, the number of Fellows was 3,104. During 1912, 184 Fellows were elected, and 7 have been reinstated, the gross total being 3,295. The Society has lost 33 Fellows by death, 52 have resigned, 1 has been elected an Honorary and Foreign Member, the elections of 4 Fellows have become void, and 47 Fellows have been removed for non-payment of Annual subscriptions.

The total number of Fellows, therefore, on the 31st December, 1912, was 3,158, showing a net increase of 54 over the preceding year. The number of Fellows elected during 1912 exceeds the average for the past six years by 21 Fellows, and the small net increase in the number of Fellows is accounted for by the large number of resignations and of Fellows removed for non-payment of Annual Subscriptions.

The names of the deceased Fellows, with the dates of their election, are:

George Attwood (1872).	William Frederick Laycock (1890).
Alfred Edward Beanes (1902).	Theodore David Lichtenstein (1878).
Andrew Heggie Black (1879).	Charles William Low (1884).
Robert Holford Macdowall Bosanquet (1865).	John McArthur (1887).
John Macdonald Cameron (1875).	William Masters (1873).
Miles Coupe (1905).	Henry de Mosenthal (1890).
Edward Divers (1860).	Benjamin Edward Reina Newlands (1864).
Arthur Edward Ekins (1883).	John Pattinson (1863).
Algernon John Elkington (1911).	B. Venkata Rao (1911).
John Oliver Ferrier (1902).	Arthur Richardson (1883).
Angus Fraser (1867).	Henry Salt (1863).
Thomas Griffiths (1879).	Henry Seward (1870).
Alexander Hill (1882).	William Robert Rigg Starling (1906).
Reginald Howell (1880).	James Pim Strangman (1887).
Otis Coe Johnson (1897).	John Wade (1890).
Humphrey Owen Jones (1900).	William Ord Wootton (1908).
David Skinner Kemp (1867).	

The following Fellows have resigned:

James Herry Allan.	William Salvador Curphey.
Allan Baguley.	Frederick Davis.
John Augustus Hermann Brincker.	Henry Wilson Davis.
Arthur Brooke.	Arthur William Eastwood.
John Coggin Brown.	Vincent Edwards.
John Arthur Carpenter.	Nevil Norton Evans.
William Clacher.	John Edwin Farmer.
George Bertram Cockburn.	Reginald Williams Ferguson.
William Cormack.	John Thomas Fox.
Samuel Herbert Cox.	Gilbert Gunn.
	Thomas Hartley.

William Pellew Harvey.  
 Alfred Kirby Huntington.  
 George Wasbington Kilner.  
 Stephen Joshua Lett.  
 Arthur Thomas McDougall.  
 Antholl Francis McEwen.  
 Alwyne Harcourt Meade.  
 Frederick Norton Kay Menzies  
 Christian Müller.  
 Herbert Simpson Newbould.  
 Frederick Norrington.  
 Robert Cecil Owen.  
 Herbert Spindler Pullar.  
 William Ralston.  
 John Armstedt Ray.  
 David Gibson Riddick.

James Beglar Robinson.  
 John Robinson.  
 Francis Murray Rogers.  
 William Saunders.  
 Alfred Henry Scholefield.  
 Frederick William Skirrow.  
 Henry George Stacey.  
 Samuel Stansfield.  
 William Scott Tebb.  
 John Traquair.  
 Stephen Herbert Trimen.  
 Herbert Wood Watson.  
 Thorp Whitaker.  
 \* Frederick Louis Wilder.  
 William Arthur Reginald Wilks

\* Since reinstated

At the end of 1911 the number of Honorary and Foreign Members was 31. Since that date the Society has mourned the loss of Lecoq de Boisbaudran and J. W. Mallet, whilst on March 7th, 1912, P. A. Guye, T. B. Osborne, P. Walden, and R. Willstätter were elected. The total number of Honorary and Foreign Members, therefore, at the present time is 33.

The Council has great pleasure in offering hearty congratulations to the following, who, in 1912, attained their Jubilee as Fellows:

William Esson, elected May 1st, 1862.  
 William Adam Dixon, elected Dec. 18th, 1862.  
 Edmund James Mills, elected Dec. 18th, 1862.

The Council desires to record its high appreciation of the services rendered to the Society over a period of eight years by the retiring Senior Secretary, Professor Crossley. Professor Crossley's tenure of this arduous office has been distinguished by great administrative skill, by sound judgment, and by unflinching tact. The Society is deeply indebted to him for the generous manner in which he has placed his time and energies at its disposal.

During the year, 336 scientific communications were made to the Society, 256 of which have been published already in the Transactions, and abstracts of all have appeared in the Proceedings.

The volume of Transactions for 1912 contains 2,568 pages, of which 2,431 are occupied by 266 memoirs, the remaining 137 pages being devoted to the Obituary Notices, the Becquerel, Cannizzaro, and Moissan Memorial Lectures, the Report of the International

Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 259 memoirs which occupy 2,270 pages.

The Journal for 1912 contains 5,497 abstracts, which extend to 2,264 pages, whilst the abstracts for 1911 numbered 5,236, and occupied 2,200 pages. The abstracts may be classified as follows:

## PART I.

	Pages.	No. of Abstracts.
Organic Chemistry .....	1,044	1,796

## PART II.

General and Physical Chemistry .....	1,238
Inorganic Chemistry .....	493
Mineralogical Chemistry .....	120
Physiological Chemistry .....	737
Chemistry of Vegetable Physiology and Agriculture .....	385
Analytical Chemistry .....	728
	<hr/>
	1,220
	<hr/>
Total in Parts I. and II .....	2,264
	<hr/>
	5,497

The possibility of Fellows resident abroad procuring through the Society fuller abstracts of papers than appear in the Journal has been under consideration, and the Council has decided:

"That persons requiring expanded Abstracts or translations of papers published in other Journals should apply to the Editor. Ten shillings per printed page (about 500 words) will be charged, and payment should be made to the Editor at the time the request for a translation or fuller abstract is forwarded to him."

The Council has also resolved:

"That in order to obtain a more equal division of abstracts, those of Physiological Chemistry and the Chemistry of Vegetable Physiology and Agriculture shall, in future, be included in Part I. of the Abstracts, instead of in Part II."

Volume V. of the Collective Index of the Journal and Proceedings of the Chemical Society (1903--1912) will be issued in two parts: Part I (Author Index) in 1913, and Part 2 (Subject Index) in 1914. Such prompt publication of the Collective Index is rendered possible by the system employed for the preparation of the



Annual Indexes, as the work done in connection with the latter can be largely utilised for the Collective Index.

The Transactions for 1912 contain Obituary Notices of Waltham Spring and Louis Joseph Troost, Honorary and Foreign Members. Obituary Notices also appear of John Attfield, John Muter, and Nevil Story-Maskelyne, and the Council expresses its thanks to those gentlemen who have kindly prepared these notices.

The Society was represented at the funeral of the late Lord Lister by the President.

Since the last Report was published, the Society has had the privilege of listening to an account of the life and work of:

- (a) S. Cannizzaro, from Sir William Tilden.
- (b) H. Moissan, from Sir William Ramsay.
- (c) H. Becquerel, from Sir Oliver Lodge.

The Council has considered the desirability of issuing a second volume of Memorial Lectures, and has decided to postpone the publication until after the delivery of the Ladenburg Lecture by Prof. Kipping and the Van't Hoff Lecture by Prof. James Walker, both of which lectures, it is hoped, will be delivered before the close of the present Session.

The President, Professor P. F. Frankland, was the official representative of the Society at the celebration, in July, 1912, of the 250th Anniversary of the Foundation of the Royal Society, when an address of congratulation was presented on behalf of the Chemical Society. The text of the address appeared in the Proceedings, Vol. 28, p. 248.

The Eighth International Congress of Applied Chemistry held in Washington and New York in September, 1912, was attended by Dr. M. O. Forster, Sir William Ramsay, and Sir Boverton Redwood as delegates of the Chemical Society.

The Society was represented at the Centenary Anniversary of the Academy of Natural Sciences of Philadelphia in March, 1912, by the late Professor J. W. Mallet and by Professor Alexander Smith; at the Bicentenary Festival of the Medical School, Trinity College, Dublin, in July, 1912, by Professor G. T. Morgan; and at the 25th Anniversary Celebration of the Verein Deutscher Chemiker by Dr. R. Messel.

During the Summer Vacation of 1912 the Society's Rooms were redecorated throughout. After consultation with the architect originally responsible for the scheme of ventilation in the Meeting Room, the Council also decided to place a large suction-fan in the roof over the Library, directly connected with the ventilating flues of the Meeting Room. This has had the result of materially improving the atmosphere of the room.

A conference of representatives of those Chemical Societies in Great Britain publishing abstracts of papers appearing in other Journals is taking place, at the suggestion of the Council, to consider the possibility of decreasing the cost of production of such abstracts. Delegates have been appointed by the various Societies as follows:

*Society of Chemical Industry.*—R. Messel, J. Lewkowitch.

*Society of Public Analysts.*—L. Archhutt, H. D. Richmond, O. Hehner.

*Institute of Brewing.*—J. L. Baker, A. R. Ling.

*Institute of Metals.*—W. Rosenhain, G. S. Scott.

*Society of Dyers and Colourists.*—E. Knecht, W. M. Gardner.

*Iron and Steel Institute.*—J. E. Stead, G. C. Lloyd.

The Council Meetings of the International Association of Chemical Societies held in Berlin in April, 1912, were attended by the three representatives of the Society, Professor A. W. Crossley, Professor P. F. Frankland, and Sir William Ramsay, and an account of the work of the Council appeared in the Proceedings for 1912 (p. 201). The General Expenses of the Association for the previous year amounted to £60, of which sum the share of the Chemical Society was £10 6s. 7d.

The next meetings of the Council will be held in London during September, 1913, and the Officers of the Association are:

Sir William Ramsay, *President*.

Prof. Percy F. Frankland, *Vice-President*.

Prof. Arthur W. Crossley, *General Secretary*.

who remain in office until the end of the meeting.

The Society has received through Sir Edward Thorpe the Annual Report of the International Committee on Atomic Weights, 1913, together with a Table of Atomic Weights. The Report appears in the Proceedings, p. 213, and in the Transactions, p. 1829.

The Council has made a further donation of £10 to the International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological.

In the last report it was mentioned that it was proposed to raise a Memorial to the late Prof. J. H. van't Hoff, and that subscriptions would be received by the Treasurer. The sum of £65 4s. was subscribed by Fellows and forwarded to the Memorial Committee.

The Council has considered a request from the Director of the Municipal Laboratory of Paris for permission to arrange for the preparation of a French translation of the Annual Reports, and has agreed to the proposition. The publication of the work will be carried out by Messrs. Hermann et Fils, of Paris.

## INCOME AND EXPENDITURE ACCOUNT

Income.		£	s.	d.	£	s.	d.
To Life Compositions ... ..					386	0	0
„ Admission Fees ... ..					692	0	0
„ Annual Subscriptions—							
Received in advance, on account of 1912 ... ..		282	0	0			
„ during 1912 ... ..		4471	0	0			
„ „ „ „ 1911 ... ..		354	0	0			
„ „ „ „ 1905-10 ... ..		18	0	0			
		3075	0	0			
Less amount included in last year's Income, being valuation of							
Arriars as per last Balance Sheet ... ..		360	0	0			
		4715	0	0			
Add Arriars at date: 1912 £448; 1911 £20; 1910 £13, estimated to realise as per Balance Sheet ... ..		350	0	0			
					5061	0	0
„ Lady Subscribers ... ..					0	0	0
„ Investments:—							
Dividends on £6750 Metropolitan Consolidated 2½ per cent. Stock ...		221	16	4			
„ £1000 London and North Western Railway 3 per cent. Debenture Stock ...		20	13	2			
„ £1350 Lda. 3d. Canliff Corporation 3 per cent. Stock ...		42	19	4			
„ £1400 India 2½ per cent. Stock ... ..		35	19	4			
„ £2400 Bristol Corporation 2½ per cent. Debenture Stock ...		56	10	6			
„ £4311 Midland Railway 2½ per cent. Preference Stock ...		102	3	10			
„ £1300 Leeds Corporation 3 per cent. Stock ... ..		33	18	0			
„ £1500 Transvaal 3 per cent. Guaranteed Stock 1923/25 ...		42	7	6			
„ £1200 North British Railway 3 per cent. Debenture Stock ...		33	18	0			
„ £700 Canada 2½ per cent. Stock 1900/05 ... ..		23	1	6			
„ Income Tax Recovered ... ..		36	13	10			
„ Interest on Deposit Account ... ..		16	16	9			
					672	17	0
„ Publications:—							
Sales:							
Journals ... ..		916	17	6			
Proceedings ... ..		47	14	9			
General Index ... ..		20	6	0			
Library Catalogue ... ..		1	7	0			
List of Fellows ... ..		4	0	0			
Atomic Weight Tables ... ..		0	9	2			
Jubilee Volume ... ..		0	5	6			
Annual Reports on Progress of Chemistry ... ..		185	8	11			
		1176	8	10			
Less Publishers' Commission ... ..		108	17	3			
		1067	11	1			
„ Proceeds of Advertisements in Journal ... ..		£205	18	10			
Less Commission ... ..		13	10	10			
		192	6	0			
„ Sale of Waste paper, etc. ... ..					125	17	1
„ Subscriptions from other Societies:—					2	15	2
Society of Chemical Industry ... ..		0	9	0			
Society of Public Analysts ... ..		11	0	6			
Optical Society ... ..		10	10	0			
British Science Guild ... ..		3	4	0			
Institute of Chemistry ... ..		1	1	0			
					26	4	1
					£2192	12	3

I have examined the above Accounts with the Books and Vouchers of the Society, and the Investments.

23, QUEEN VICTORIA STREET, E.C.4.  
2nd March, 1913

W. B. KEEN,  
Chartered Accountant

FOR THE YEAR ENDED 31ST DECEMBER, 1912.

*Expenditure.*

	£	s.	d.	£	s.	d.
By Expenses on account of Journal and Proceedings:—						
Salary of Editor, including indexing .....	570	0	0			
Salary of Sub-Editor .....	280	0	0			
Editorial Postages .....	31	1	4			
Abstracters' Fees .....	546	10	3			
Printing of Journal .....	2953	10	1			
Binding .....	69	15	8			
Printing of Advertisements .....	52	2	6			
Printing and Addressing .....	119	19	5			
Distribution of Journal .....	628	13	4			
Authors' Copies .....	192	19	5			
Insurance of Stock at Clay's .....	6	4	3			
Printing of Proceedings .....	218	12	5			
Binding .....	8	15	8			
Distribution .....	44	9	3			
				5633	12	7
Annual Reports on the Progress of Chemistry .....				412	6	0
Purchase of back numbers of Journal .....				7	12	1
List of Fellows .....				72	7	9
Library Expenses:—						
Salary of Librarian and Assistant .....	190	12	0			
Books and Periodicals .....	246	12	3			
Binding .....	25	4	7			
Bookcases .....	14	19	4			
				477	8	2
Indexing for International Catalogue .....				39	0	0
Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Techno- logical .....				10	0	0
International Association of Chemical Societies .....				10	6	7
Administrative Expenses:—						
Salary of Assistant Secretary .....	220	0	0			
Salary of Office Assistant .....	81	3	6			
Wages (Commissionaire, Housekeeper, and Charwoman) .....	156	15	6			
Coal and Lighting .....	41	18	2			
House Expenses and Repairs .....	36	9	6			
Tea Expenses .....	29	14	0			
Insurances .....	11	9	3			
Accountants' Charges .....	21	0	9			
Commission on Recovery of Income Tax .....	1	16	8			
Printing .....	127	1	0			
Stationery .....	56	1	5			
Postages .....	163	2	11			
Unrecovered Address .....	3	3	0			
Miscellaneous Expenses .....	25	7	1			
				1287	17	8
Balance, being excess of Income over Expenditure, carried to Balance Sheet .....				476	1	7

£5120 12 3

I certify them to be in accordance therewith. I have also verified the Balance at the Bankers.

Approved— JOHN M. THOMSON,  
SAMUEL RIDGALL,  
JAMES J. DOBBIE



PAID IN ADVANCE AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1912.

[illegible]

I have examined the above Account with the Books and Vouchers of the Society and certify it to be in accordance therewith.

Approved—  
W. F. REYNOLDS, Treasurer.

I have also verified the Balance at 2003 with the Treasurer, and find it correct.

Approved—  
JAMES J. BOBBLE, Chairman.

$$\begin{aligned} \mathbf{r}(t) &= \mathbf{r}_0 + \mathbf{v}_0 t + \frac{1}{2} \mathbf{a}_0 t^2 \\ \mathbf{v}(t) &= \mathbf{v}_0 + \mathbf{a}_0 t \\ \mathbf{a}(t) &= \mathbf{a}_0 \end{aligned}$$

## Appendix

have also verified the Balance at  
 JAMES M. THOMSON,  
 CHARLES W. WEAVER,  
 JAMES J. LEBLANC.

At the request of the Rev. W. G. Searle, Keeper of Coins at the Fitzwilliam Museum, Cambridge, the Council has presented to the Museum copies of the Longstaff Medal and Faraday Medal.

The number of books borrowed from the Library during the year was 1,825, as against 1,808 during the previous year; of these 491 were issued by post, as against 419 in the preceding year.

The additions to the Library comprise: 135 books, of which 70 were presented; 482 volumes of periodicals (representing 237 journals), and 76 pamphlets; as against 171 books, 438 volumes of periodicals (representing 237 journals), and 87 pamphlets last year.

The Library is indebted to Mr. J. A. Audley for a welcome gift of early journals.

The yearly increasing size of the Library will necessitate the consideration in the immediate future of the provision of adequate accommodation for its growth. In a statement of the Librarian appended to the President's Address in 1890, it was recorded that the Library then contained 9,884 volumes, made up of 3,082 volumes of systematic works, and 6,802 periodicals, with the addition of 1,450 pamphlets. At the present time it is estimated that the Library contains 21,256 volumes, of which 5,983 are systematic works, 15,273 volumes of periodicals, together with 3,500 pamphlets. It is thus seen that in twenty-two years the periodicals in the Library have increased in number of volumes by 134·5 per cent., the systematic works by 91 per cent., and the general total by 115 per cent.

It is estimated that shelf-room for 7,000 volumes will be required to accommodate the increase of volumes for the next ten years. At the close of 1913 there will at least be an additional 650 volumes to accommodate, whilst the empty shelving now at liberty will only contain some 250 volumes. Therefore, not only for the future, but also for the immediate present, additional Library accommodation is essential, and the Council has referred this question to the House and Library Committees.

Taking into account the occurrence of some items of exceptional expenditure, such as the decoration of the whole building and the ventilation of some of our rooms, it is satisfactory to find that, after meeting these expenses out of the income for the year, there is still an excess of income over expenditure of £176 1s. 7d. In 1913 the needs of the Library in the direction of providing accommodation for its continuous growth will necessarily entail considerable outlay, as pointed out above. For 1912 the income from all sources amounted to £8120 12s. 3d., and the expenditure to £7944 10s. 8d.; for 1911 the corresponding amounts were £7735 11s. 6d. and £7499 3s. 10d. respectively. In other

words, our income has increased by £385 0s. 9d., and our expenditure by £444 16s. 10d. The redecoration, improvements in ventilation, etc., alone account for £265 of this, and the increase in cost of the *Journal* for £124 2s. 8d.

As it was found impossible without either realising some of our investments or raising the annual subscription to give to Fellows without charge Vol. V. of the Collective Index, the price charged for it (thirty shillings) was fixed so as to cover as nearly as possible the cost of printing and distribution. The cost of preparing the index for the press is included in the editor's salary, and under the new arrangements its publication has been arranged for with an expedition hitherto impossible. From the number of Fellows who have applied and the number of copies which we may reasonably hope to sell to the public through our publishers, it seems probable that this volume of the Collective Index will not entail any serious outlay on the part of the Society.

The net income of the Research Fund for the year amounted to £367 6s. 5d., and by drawing on the balance in hand to the extent of £15 3s. 7d., grants were made amounting in all to £361, whilst the Longstaff Medal and Honorarium accounted for the remaining £21 10s.

A Vote of Thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year, proposed by Mr. W. F. REID, seconded by Mr. A. CHASTON CHAPMAN, was acknowledged by Professor ARTHUR W. CROSSLEY.

The PRESIDENT then delivered his address entitled "The Walden Inversion." Sir WILLIAM TILDEN proposed a Vote of Thanks to the PRESIDENT, coupled with the request that he would allow his address to be printed in the *Transactions*. The motion was seconded by Professor HAROLD B. DIXON, and acknowledged by the PRESIDENT.

The Report of the Scrutators was presented, and the President declared that the following had been elected as Officers and Council for the ensuing year:

*President:* William Henry Perkin, Sc.D., LL.D., F.R.S.

*Vice-Presidents who have filled the Office of President:* Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Bailly Dixon, M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.;



Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, D.Sc., LL.D., F.R.S.; Hugo Müller, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; the Rt. Hon. Sir Henry Enfield Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., F.R.S.

*Vice-Presidents:* Herbert Breerton Baker, M.A., D.Sc., F.R.S.; George Thomas Beilby, LL.D., F.R.S.; Horace Tabberer Brown, LL.D., F.R.S.; Edmund James Mills, D.Sc., LL.D., F.R.S.; Gilbert Thomas Morgan, D.Sc.; William Jackson Pope, M.A., F.R.S.

*Treasurer:* Alexander Scott, M.A., D.Sc., F.R.S.

*Secretaries:* Samuel Smiles, D.Sc.; James Charles Phillip, M.A., D.Sc., Ph.D.

*Foreign Secretary:* Arthur William Crossley, D.Sc., Ph.D., F.R.S.

*Ordinary Members of Council:* George Barger, M.A., D.Sc.; Edward John Bevan; William Robert Boustfield, M.A., K.C.; Adrian John Brown, M.Sc., F.R.S.; Harold Govett Colman, D.Sc., Ph.D.; Frederick George Donnan, M.A., Ph.D., F.R.S.; Arthur Hardeu, D.Sc., Ph.D., F.R.S.; Thomas Martin Lowry, D.Sc.; Hugh Marshall, D.Sc., F.R.S.; Kennedy Joseph Previté Orton, M.A., Ph.D.; Sir Boverton Redwood, Bart., D.Sc.; Edward John Russell, D.Sc.

## PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 14th, 1913.

By PERCY FARADAY FRANKLAND, Ph.D., LL.D., ScD., F.R.S.

*The Walden Inversion.*

In the Pasteur Memorial Lecture which I had the honour to deliver in this room sixteen years ago, I made the following statement:

"Before leaving the subject of malic acid, it is worthy of note that it is in connection with this acid that undoubtedly one of the most important discoveries relating to optically active bodies has been made since the time of Pasteur; I refer to the remarkable transformation of levomalic acid into dextromalic acid, and *vice versa*, through the medium of the corresponding chlorosuccinic acids, which has been accomplished by Walden (*Ber.*, 1896, **29**, 133).

*l*-Malic acid  $\rightarrow$  *d*-chlorosuccinic acid  $\rightarrow$  *d*-malic acid.

*l*-Malic acid  $\leftarrow$  *l*-chlorosuccinic acid  $\leftarrow$  *d*-malic acid."

It is with regard to this phenomenon, now so well known under the name of *Walden Inversion*, that I propose to offer some remarks to-day.

The past sixteen years have shown that the importance which I then attributed to Walden's discovery was fully justified, for this phenomenon is attracting more and more attention both from the experimental and the speculative sides.

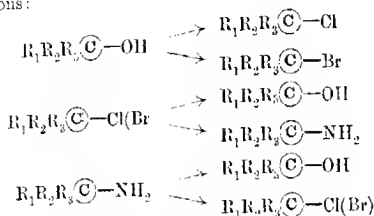
Sir Oliver Lodge, in the fascinating lecture which he recently delivered to us on the discovery of radioactivity, made the very pertinent remark that:

"A discovery of real and essential novelty can never be made by following up a train of prediction. It is often made during the process of following a clue, but the clue does not logically lead to it. . . . The discovery which has been pointed to by theory is always one of profound interest and importance, but it is usually the close and crown of a long and fruitful period; whereas the discovery which comes as a puzzle and a surprise usually marks a fresh epoch and opens a new chapter in science."

Walden's discovery was certainly a puzzle and a surprise, for it did not fit into any pre-existing theory of optical activity, and had not been anticipated as a corollary to van't Hoff's theorem of the asymmetric carbon atom. It is highly probable that it may mark

an epoch in our views with regard to the mechanism of the process of substitution in general.

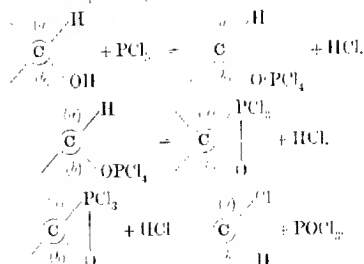
As is well known, the Walden inversion has so far only been observed in the case of the substitution of a group directly attached to the asymmetric carbon atom itself in one or other of the following transformations:



Prior to the discovery of the Walden inversion, it would have been assumed that in such a substitution the entering group would either take the place of the extruded group, in which case the configuration would remain unaltered, or that it should take up any other position *without preference*, in which case there would be formed 50 per cent. of the one enantiomorph and 50 per cent. of the other, with the result that the product would be inactive (racemisation).

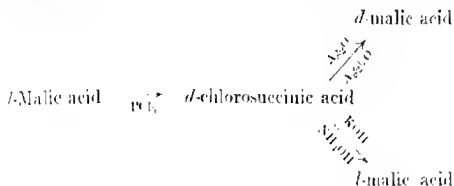
The discovery of the Walden inversion showed that in some of these substitutions there may be a *preferential* assumption of the position formerly occupied by one of the other groups,  $R_1$ ,  $R_2$ , or  $R_3$ , attached to the asymmetric carbon atom, resulting therefore in a preponderating, or, indeed, in some cases the almost exclusive, production of the enantiomorphous configuration (inversion).

Prof. Armstrong, with his characteristic resource, was the first to furnish a tentative theoretical explanation of this unexpected phenomenon (T., 1896, **69**, 1309). He suggested the formation of two intermediate compounds, thus:



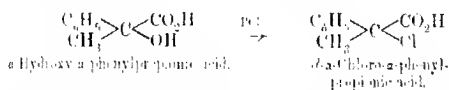
The merit of this ingenious explanation depends on its accounting for the preservation of the asymmetry of the carbon atom throughout the change without importing any new conceptions of combination or of valency.

It would, however, be difficult to apply this explanation to the optical inversions, which Walden soon discovered must take place when some bases hydroxylate a halogen acid. Thus, inasmuch as silver oxide and potassium hydroxide transform one and the same chlorosuccinic acid into the two enantiomorphous malic acids respectively, it follows as a necessary consequence that in one or other of these transformations an inversion must occur. Thus:



From the above, it is obvious that irrespectively of whether or not a configurative change occurs in the transformation of *l*-malic acid into *d*-chlorosuccinic acid, in one or other of the transformations of the latter into *d*-malic and *l*-malic acid respectively an inversion must occur (Walden and Lutz, *Ber.*, 1897, **30**, 2795; Walden, *Ber.*, 1897, **30**, 3116).

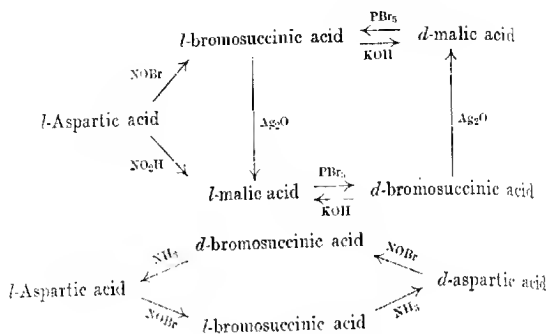
It is again obvious, also, that the above mechanism proposed by Armstrong could not be applied to the action of  $\text{PCl}_5$  on an  $\cdot\text{OH}$  group attached to a tertiary carbon-atom. Thus:



but, of course, it might be argued that in this particular case no change of configuration does actually occur (McKenzie and Clough, *T.*, 1910, **97**, 1016, 2561; 1912, **101**, 390).

The great importance of this phenomenon of optical inversion has not only led to much speculation, but fortunately also to a large amount of experimental work, for which we are indebted to Walden, Lutz, Purdie, and more especially to Emil Fischer and to McKenzie.

In a number of cases the complete cycle of changes from a given optically active compound to its enantiomorph and back again to the original compound has been realised. Thus, a single example will illustrate the beautiful symmetry of the results obtained:



This example, however, equally illustrates the difficulties with which we are confronted in attempting an explanation, for at which of the steps does the inversion occur? The fundamental difficulty is that we have at present no means of ascertaining whether a change of sign in any of the above steps betrays a change of configuration, and, conversely, we are equally ignorant as to whether identity of sign in the case of two different compounds corresponds with identity of configuration. Thus, in passing from *l*-aspartic to *d*-aspartic acid, we know that an inversion has taken place, but we do not know whether the change of configuration has occurred in passing from *l*-aspartic acid to *l*-bromosuccinic acid, or in passing from the latter to *d*-aspartic acid. Some speculations have assumed the one, and some the other hypothesis.

It is usual and convenient to designate replacement without change of configuration as *normal*, and with change of configuration, *abnormal*, and this convention will be adopted throughout the present address.

Much discussion has taken place as to which of the replacements in question are to be regarded as normal and which as abnormal, but the most painstaking examination of the data has so far failed to detect any convincing evidence bearing on the subject. I would, however, draw attention to some of the more striking regularities which appear to emerge from an examination of the known facts.

### 1.—Action of $\text{PCl}_5$ and $\text{PBr}_3$ on Hydroxy-compounds.

In practically all well-established cases, the treatment of an active hydroxy-acid with phosphorus pentachloride (or bromide) results in the production of a chloro-acid (bromo-acid), with change of sign. A similar change of sign has also been found in most cases

to accompany the action of phosphorus pentachloride on the esters of such hydroxy-acids, as far as these have been investigated.

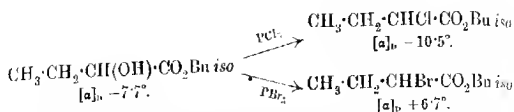
A similar change of sign has recently been observed by McKenzie (*Brit. Assoc. Reports*, 1912; this vol., p. 687) to occur when  $\text{PCl}_5$  acts on phenylmethylcarbinol with formation of phenylmethylchloromethane. This case is of particular interest, as it furnishes the first example of a Walden inversion occurring in connexion with a compound not containing either a free or esterified carboxyl group in the molecule. In the following table I have summarised the results obtained with  $\text{PCl}_5$ :

*Action of  $\text{PCl}_5$  and  $\text{PBr}_5$  on Hydroxy-compounds.*

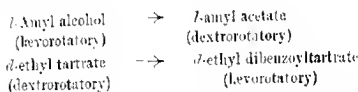
(l-Malic acid) (l-Malic esters)	$\xrightarrow{\text{PCl}_5}$	d-Chlorosuccinic acid.
(d)-Lactic acid Supposed to be really of levo-con- figuration, because it forms levorotatory salts and esters)	$\xrightarrow{\text{PCl}_5}$ $\xrightarrow{\text{PBr}_5}$	(d)-Chloropropionic acid, (d) Bromopropionic acid.
(l- $\beta$ -Hydroxybutyric Me-ester (Acid and ester have same sign))	$\xrightarrow{\text{PCl}_5}$	d- $\beta$ -Chlorobutyric Me-ester.
(l- $\beta$ -Hydroxybutyric acid (Acid and salts, levo))	$\xrightarrow{\text{PCl}_5}$	d- $\beta$ -Chlorobutyric acid.
(l-Phenylglycollic acid (Mandelic acid) l-Phenylglycollic Esters)	$\xrightarrow{\text{PCl}_5}$ $\xrightarrow{\text{PBr}_5}$	d-Phenylchloroacetic acid, d-Phenylbromooxyacetic acid.
(*) d- $\alpha$ -Hydroxy- $\beta$ -phenylpropionic acid	$\xrightarrow{\text{PCl}_5}$	(l- $\alpha$ -Chloro- $\beta$ -phenylpropionic acid.)
(l- $\alpha$ -Hydroxy- $\beta$ -phenylpropionic Esters)	$\xrightarrow{\text{PCl}_5}$	l- $\alpha$ -Chloro- $\beta$ -phenylpropionic acid.
(l- $\alpha$ -Hydroxy- $\alpha$ -phenylpropionic acid) (Atrolactic acid)	$\xrightarrow{\text{PCl}_5}$	d- $\alpha$ -Chloro- $\alpha$ -phenylpropionic acid.
(l- $\alpha$ -Hydroxy- $\alpha$ -phenylpropionic Esters)	$\xrightarrow{\text{PCl}_5}$	d- $\alpha$ -Chloro- $\alpha$ -phenylpropionic acid.
(d-Hydroxy- $\beta$ -phenylpropionic acid, (Similarly with the d-acid)	$\xrightarrow{\text{PBr}_5}$ $\xrightarrow{\text{PCl}_5}$	d- $\beta$ -Bromo- $\beta$ -phenylpropionic acid, d- $\beta$ -Chloro- $\beta$ -phenylpropionic acid.
d-Phenyl ethyl carbinol	$\xrightarrow{\text{PCl}_5}$	l-Phenylmethyl chloromethane.

\* McKenzie and Barrow (T., 1911, **99**, 1911) find that no change of sign takes place in the case of the action of  $\text{PCl}_5$  on the Ester, but they assume that a change takes place in the action on the free acid. The free d-hydroxy-acid gives with  $\text{PCl}_5$  a dextrorotatory chloro-acid chloride, which they believe to be the chloride of the l-dl-acid (see also p. 735).

Note. The following anomalous results have been recorded by Gaye and Jordan (*Bull. Soc. chim.*, 1896, [iii], **15**, 195), in which  $\text{PCl}_5$  and  $\text{PBr}_5$  appear to act differently, thus:



The great uniformity with which the action of  $\text{PCl}_5$  is attended by a change of sign naturally suggests that the use of this reagent causes an inversion of the configuration. A very slight acquaintance, however, with the changes of sign which may accompany substitutions more remote from the asymmetric carbon atom at once shows that any such sweeping conclusion would be quite unjustifiable. Thus:



are two of a very large number of examples which might be cited.

Very striking and instructive evidence as to the difficulty of connecting change of sign with change of configuration is furnished by experiments which I made in conjunction with Dr. Andrew Turnbull some thirteen years ago, but of which the results have not yet been published. We investigated the action of  $\text{PCl}_5$  on the levorotatory ethereal salts of glyceric acid, and obtained the corresponding esters of  $\alpha\beta$ -dichloropropionic acid, exhibiting the following optical relations:

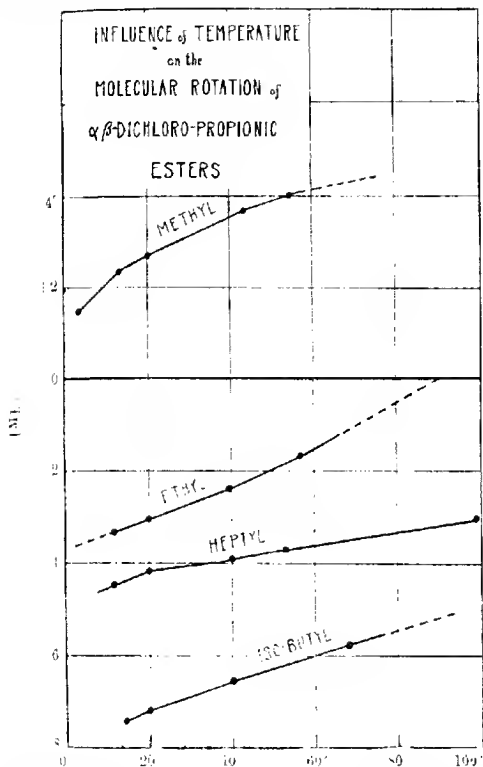
	$[\text{M}]_D^{25}$		$[\text{M}]_D^{25}$	
Methyl glycerate .....	-5.76	$\rightarrow$	Methyl $\alpha\beta$ -dichloropropionate.....	-1.96
Ethyl .....	-12.30	$\rightarrow$	Ethyl .....	-4.68
isoButyl .....	-23.05	$\rightarrow$	isoButyl .....	-7.28
Heptyl .....	23.05	$\rightarrow$	Heptyl .....	4.75

From the above it might be argued that in the case of the methyl ester  $\text{PCl}_5$  had acted abnormally (change of configuration), whilst in that of the higher homologous esters the action was normal (configuration unchanged). This argument is, however, at once seen to be untenable by a study of the influence of temperature on the rotation of the  $\alpha\beta$ -dichloropropionates.

From the diagram it will be seen that whilst rise of temperature increases the dextrorotation of the methyl ester, it diminishes the levorotation of the higher esters, whilst if the latter were of enantiomorphic configuration to the methyl ester, their levorotation would doubtless be increased by rise of temperature.

## II.—Action of Thionyl Chloride on Hydroxy-compounds.

The relations between the active hydroxy-compounds and their chloro derivatives can again be investigated by using thionyl chloride



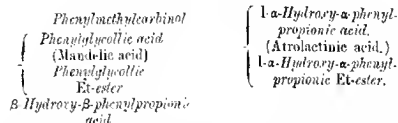
as the chlorinating agent. The following transformations are known to occur:

## With Change of Sign.



\* P. Frankland and Lea, unpublished.



*Without Change of Sign.*

Thus the existing data are quite sufficient to show that the action of  $\text{SOCl}_2$  is much more variable, from the point of view of effecting a change of sign, than is the case with  $\text{PCl}_5$ .

It is very striking that in all those cases in which  $\text{SOCl}_2$  leads to no change of sign, and therefore, as may be assumed for present purposes, also to no change of configuration, there is a phenyl group attached to the asymmetric carbon atom. Indeed, it will be seen later that the direct attachment of phenyl to the asymmetric carbon atom leads to exceptional behaviour in several different connections.

The phenomena attending the reactions brought about by  $\text{HNO}_2$  and  $\text{NOCl}$  on amino-compounds, and by  $\text{NH}_3$  and bases on halogen compounds, will be discussed later (see pp. 728, 730).

*Recent Speculations with regard to the Mechanism of the Walden Inversion.*

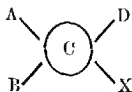
The proposals which have recently attracted most attention are those of Emil Fischer on the one hand, and of Werner on the other, and both depend on the importation of the principle of attractions exerted by the asymmetric carbon atom on groups not actually attached by the ordinary four valencies of the carbon.

The process suggested by Fischer is perhaps best appreciated by a consideration of the concrete illustrative example, the action of liquid ammonia on monobromopropionic acid, which he pictures as taking place in the following manner.

One or more molecules of ammonia become attached to the bromopropionic acid by residual affinity so as to give rise to an additive product ("polymolecule"). Then, when the bromine separates in the ionised form, the  $\text{NH}_2$ -group can either take the place of the latter, in which case there will result no change of configuration, or one of the other three groups takes the place vacated by the bromine, and the  $\text{NH}_2$  takes the place vacated by that group, with the result that inversion will have occurred (E. Fischer, *Annalen*, 1911, **381**, 132).

Werner (*Ber.*, 1911, **44**, 881), on the other hand, takes the asymmetric carbon atom with its four different groups, A, B, D, X, as forming the tetrahedron, in which X is the group that suffers

replacement. This tetrahedron will have four faces: (1) ABX,



(2) ADX, (3) BDX, and (4) ABD, towards each of which the central carbon atom may be supposed to be capable of attracting an external group. If such an external group capable of replacing X be attracted to any one of the three faces, (1), (2), or (3), contiguous to X, then the replacement will take place without configurative change; on the other hand, if the group is attracted to the plane (4), diametrically opposite to X, then replacement will result in the production of the enantiomorphous configuration.

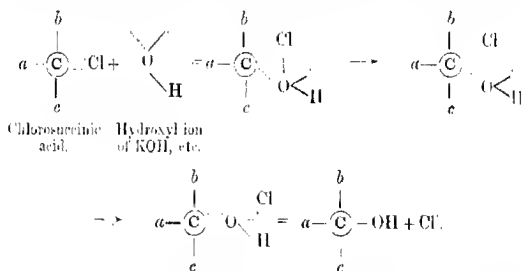
This mechanism is extremely simple in its conception, and Werner's mode of expression perfectly clear and definite. It postulates that by the mere attraction of the external group to any of the three faces (1), (2), and (3), the original configuration is already guaranteed before the removal of X, whilst if the attraction be to the face (4), then the opposite configuration is similarly ensured. The mechanism involves no reference to one group taking the place of another, for as a matter of fact the entering group will not in the first instance, nor doubtless even in the condition of final equilibrium, take up the exact position previously occupied by any other group present in the original molecule. It is only the configuration, which in three cases will be the same, and in the fourth case the opposite of the original configuration.

It appears to me that the mechanisms suggested by E. Fischer and by Werner are essentially the same, the differences being, for the most part, only differences of terminology. There is, however, a special merit about the Werner picture, inasmuch as it emphasises an important property of the tetrahedral model representing the asymmetric carbon, to which I do not think that attention had been hitherto called, namely, that with regard to a given group X attached to the carbon atom there are *four* positions towards which a fifth group can become attracted by the carbon atom, and that of these four positions three are identical, and one different from the point of view of the configuration resulting when the group X is eliminated.

The more general terms in which the Fischer mechanism is formulated appear to me, however, to have one advantage. Fischer distinctly says that it is by no means necessary that the attracted group (for example,  $\text{NH}_2$ ) should be attached to the carbon atom (*Annalen*, 1911, **381**, 132), but that it *may be attached to one of the four substituents* (*Annalen*, 1912, **394**, 352), the essential being

that it should belong to the molecule. I think that this reservation is of importance, and likely to commend itself to chemists, as it is just in the case of a saturated atom of carbon (as the asymmetric carbon atom must of necessity be) that we have least right to postulate its possession of residual affinity. It is, moreover, highly significant that the groups attached to the asymmetric carbon which suffer replacement in the reactions with which we are concerned are precisely of such a kind (halogens, hydroxyl,  $\text{NH}_2$ ) that we can safely predicate their possession of residual affinity in a high degree. It would appear therefore much more reasonable to suppose that the reagent is attracted by the residual affinity of a group which is known to possess it than by the residual affinity of the saturated atom of carbon, which very possibly does not possess any. The bearing of this on the phenomena of substitution in general is sufficiently obvious.

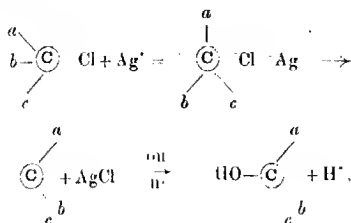
Yet another mechanism depending on the idea of residual valency has been proposed by J. Gadamer (*Chem. Zeit.*, 1910, **34**, 1001; 1912, **36**, 1327). Gadamer emphasises the necessity for assuming the formation of intermediate compounds in order to preserve continuous asymmetry during the process of substitution, and he illustrates the possibility of substitution occurring with and without change of configuration by the case of chlorosuccinic acid, in which the action of a *cation* (for example, silver) is supposed to lead to change of configuration, whilst the action of an *anion* (for example, hydroxyl) is attended with no change of configuration. Thus:



(N.B.—The divisibility of valency is indicated by a sheet of dotted lines. The tendency of oxygen to become quadrivalent is also indicated by dotted lines.)

Thus the substitution of Cl by OH in the above scheme takes place without change of configuration. On the other hand, when the silver salt of chlorosuccinic acid is heated with water, the substitution of Cl by OH takes place according to the following scheme.

in which the attack of the silver ion on the chlorine is the primary cause of the reaction:



In this process the chlorine is gradually withdrawn from the sphere of attraction of the carbon by the silver cation, and the other three groups (*a*, *b*, *c*), tending to set themselves in a plane with the carbon atom, leave the region opposite to the chlorine vacant for the attachment of the anion OH<sup>-</sup>, the substitution being thus accomplished with change of configuration.

In my opinion, the mechanism suggested by Gadamer in the case of the anion is really the same as that of Fischer and more especially of Werner, inasmuch as it is merely an elaboration of the idea that the OH<sup>-</sup>, if attracted to one or other of the three planes adjacent to the Cl, necessitates replacement without change of configuration. On the other hand, Gadamer's scheme for the change of configuration resulting from the action of the cation appears to me to possess some elements of novelty, although it is in no way excluded by, or inconsistent with, the schemes of E. Fischer and Werner.

A most ingenious model illustrating this mode of effecting a change of configuration has been devised by my pupil and collaborator, Mr. Garner, who developed the idea quite independently of Gadamer.

This model, as well as the one described by Garner (*P.*, 1912, **28**, 65) a year ago, appear to me to be by far the best yet devised for illustrating some of the remarkable properties of the asymmetric carbon atom.

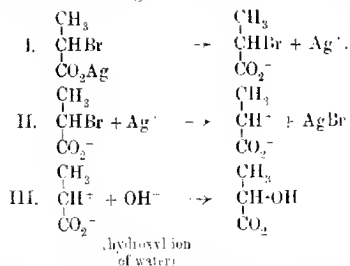
A very interesting consideration is raised by Gadamer, who points out that the preservation of optical activity in the substitution of a group attached to an asymmetric carbon atom is inconsistent with the old idea of one group replacing another, for that would involve a momentary attachment of only three groups, which would immediately lead to the production of a symmetric system (the three groups falling into one plane with the carbon atom), and by addition of a new group to this system racemisation should occur.

Gadamer, however, does not definitely discard the old idea of substitution, but accounts for the preservation of the activity by assuming that if the asymmetry is preserved without change of configuration, then the new group must have become attached before the three groups have swung into one plane with the carbon atom, and if the asymmetry is preserved with change of configuration, then the new group must have become attached at a moment when the three groups have through their momentum swung beyond the position in which they are in one plane with the carbon atom.

It appears to me much preferable to avoid this highly fanciful picture, and to assume that in a substitution the entering group becomes potentially attached to the carbon atom (either on one of the three planes adjacent to or on the plane diametrically opposite to the extruded group) *before the extruded group is actually detached*. This much simpler conception makes the fact of the retention of optical activity when substitution takes place at an asymmetric carbon atom serve as a demonstration of the truth of the idea which has so long been favoured by many chemists that addition of some kind must invariably precede substitution.

These considerations also lead up to the very interesting question of whether optical activity can be preserved in the case of an asymmetric system becoming ionised at the central atom.

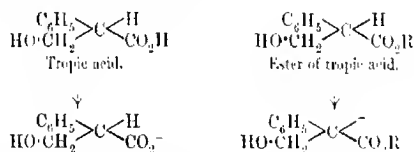
That the ionisation of a group attached to an asymmetric carbon atom does not in general arise depends on the circumstance that an atom of carbon attached to four different groups cannot be the essential part of an electrolyte; but in the case of the halogen fatty acids some ionisation of the halogen atom, and therefore of the residual group, is often considered probable; thus Billmann (*Annalen*, 1911, 388, 338) supposes the transformation of silver  $\alpha$ -bromopropionate into  $\alpha$ -hydroxypropionate in aqueous solution to take place in the following manner:



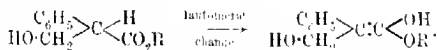
Inasmuch as the activity is preserved in the above transformation, it follows that these reactions involve the preservation of asymmetry.

in the amphoteric ion figured in II and III. I imagine that some chemists would condemn the above explanation of the reaction on the ground that the supposed ionisation would lead to inactivity. In the classical investigations of Pope and Peachey and of Smiles on the optically active derivatives of sulphur, selenium, and tin, many of the compounds had their rotatory power determined in the ionised state, with the asymmetric atom involved in the ionisation.\* There is therefore abundant evidence that a tetravalent asymmetric atom can retain its asymmetry in the ionised condition. There is, however, also very striking evidence that the asymmetry in such cases is very unstable, and, indeed, the racemisation phenomena exhibited by the optically active tin compounds described by Pope and Peachey (P., 1900, 16, 42, 116) are extremely remarkable, and quite unlike anything encountered in the case of the optically active compounds of carbon.

It has been suggested that evidence of ionisation at an asymmetric atom being a cause of racemisation is furnished by the different behaviour of tropic acid and its esters in respect of racemisation by OH-ions. Thus, Gadamer and Kuntze have found (*Chem. Zvt.*, 1910, 34, 1004) that whilst the esters of tropic acid are readily racemised, the acid itself is not racemised by OH-ions. Gadamer attributes this difference to the acid being ionised at the CO<sub>2</sub>H group, whilst the ester, which is a pseudo acid, only becomes ionised in the presence of OH-ions, thus:



It would, however, appear probable that the ionisation of the ester should be preceded by tautomeric change, which would alone destroy the asymmetry, thus:



That an ionised quadrivalent atom should be capable of preserving its asymmetry is not so surprising, if ionisation be regarded as resulting from the combination of the electrolyte with the

\* Pope and Harvey (T., 1901, 79, 831 and Jones (T., 1904, 85, 229) have also found very rapid auto-racemisation in the case of optically active ammonium iodides, but, as this takes place in non-ionising solvents, they attribute the change to decomposition of the ammonium salt into tertiary amine and alkyl iodide followed by recombination.

maximum number of water molecules which it can hold by means of the residual valency of the oxygen (P. Frankland, *Nature*, 1904, 70, 222). Nor is it surprising that these comparatively loosely bound water molecules (which are doubtless not permanently attached but continually undergoing alternate dissociation from and reunion with the ion) should cause the asymmetry to be of a more ephemeral character than when they are replaced by a univalent group permanently attached in the ordinary way. Indeed, their alternate dissociation from and reunion with the ion will possibly give opportunity to a series of changes in configuration (Walden inversion), which will sooner or later lead to the complete racemisation of the ion. In fact, the above conception of ionisation as being caused by union of the electrolyte with water indicates that electrolytic dissociation and reassociation must be regarded as essentially processes of substitution, and, if these processes take place at an asymmetric atom, opportunities will be afforded for their being attended by configurative change.

There is thus a remarkable agreement between the several more plausible explanations which have been suggested with regard to the mechanism whereby the Walden inversion may occur, but unfortunately all the attempts which have hitherto been made to apply these explanations to specific cases have proved singularly unfruitful.

Thus, Walden originally suggested that the action of  $\text{PCl}_5$  was normal, and that in the hydroxylation of the resulting chloro-compound the action of  $\text{KOH}$  was also normal, but that of  $\text{AgOH}$  abnormal (that is, caused change of configuration).

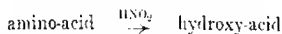
Bilimann (*Annalen*, 1911, 388, 335), on the other hand, has indicated what appears to be an intrinsic difference between the hydroxylation of a halogen acid by means of  $\text{KOH}$ , on the one hand, and by  $\text{AgOH}$  on the other. In the former case the process is dependent on the action of  $\text{OH}^-$  ions, and in the latter to  $\text{Ag}^+$  ions. The difference is attributed to the difference between the potassium and the silver salts of the halogen acid. The hydroxylation of the potassium salt is usually very slow, whilst that of the silver salt is generally very rapid, depending, as it is supposed to do, on the attack of the silver ion on the halogen with formation of insoluble, and therefore undissociated, silver haloid. That the undoubted occasional difference between the configuration of the hydroxyacid obtained, according as  $\text{KOH}$  or  $\text{AgOH}$  is employed for the hydrolysis, may be connected with the soluble and ionised nature of the  $\text{K}$ -haloid, on the one hand, and the insoluble and non-ionised  $\text{Ag}$ -haloid on the other, is rendered the more probable, as Bilimann points out, inasmuch as  $\text{HgO}$  has been found to yield the same

hydroxy-acid as  $\text{AgOH}$ , and the  $\text{Hg}$ -haloids, as is well known, are but very slightly ionised in solution.\*

The great difference in the mode of hydrolysis of the alkaline and silver salts of halogen acids has also been established by the important investigations of Senter (T., 1907, **91**, 460; 1909, **95**, 1837; 1910, **97**, 346; 1911, **99**, 95, and later).

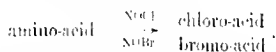
Gadamer, again, bases his speculations, as we have seen, on the action of  $\text{OH}$ -ions in the case of  $\text{KOH}$ , and on that of  $\text{Ag}$ -ions in the case of  $\text{AgOH}$ ; but this harmony between Büllmann and Gadamer is only superficial, for whilst Büllmann draws the inference that the  $\text{Ag}$ -ions probably lead to hydrolysis without change of configuration, Gadamer comes to precisely the opposite conclusion.

Another endeavour is made by Büllmann to connect the supposed mechanism of the Walden inversion with specific instances of the phenomenon. Owing to the rapid and straightforward action of nitrous acid on amino-acids, he assumes that the transformation:



occurs without change of configuration. I would suggest that this hypothesis is favoured by the consideration that both the aspartic and the malic acid which occur in the vegetable kingdom are likely to have the same configuration, and that, as a matter of fact, the natural malic acid is the one which is produced by the action of nitrous acid on natural aspartic acid.

By analogy, also, he assumes that  $\text{NOCl}$  and  $\text{NOBr}$  react on amino-acids without change of configuration:



On the other hand, Büllmann thinks that in the action of  $\text{NOCl}$  and  $\text{NOBr}$  on the esters of aminoacids, a configurative change may occur because, in the action of nitrous acid on aminoacetic ester, diazoacetic ester is actually formed, thus indicating that the diazo-group can, in the case of the ester of the amino-acid, actually come into connexion with the asymmetric carbon atom itself. (If the diazo-ester were actually formed, of course, complete racemisation should occur, because in the diazo-ester the asymmetry is lost, thus:

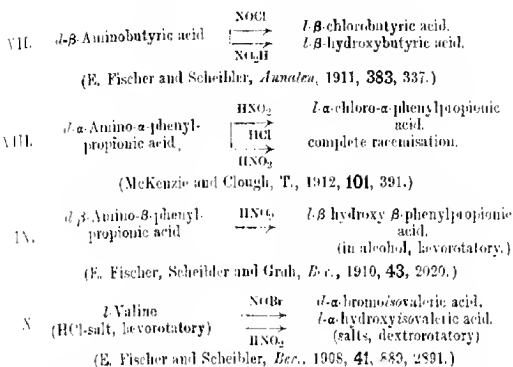


Then, if it be assumed that in the case of  $\text{NOCl}$  or  $\text{NOBr}$  the

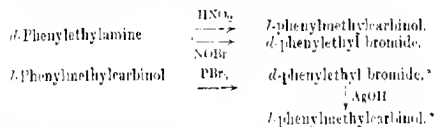
\* Of great importance in this connexion are the investigations of Walden (B., 1890, **32**, 1833) on the action of a whole series of bases on the halogen-succinimide, and by McKenzie and Clough (T., 1909, **95**, 779) on the action of a similar series of bases on phenylchloroacetic acid.







*Note.*—The following transformations recently obtained by Holmberg (*Ber.*, 1912, **45**, 1003) are of interest:



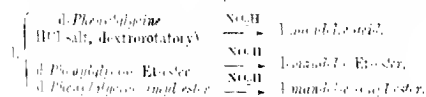
\* The rotations are given as somewhat uncertain. (See also Marekwald and Meth, *Ber.*, 1905, **38**, 591.)

Thus in all the cases investigated, the action of NOBr on the free amino-acid yields a bromo-acid of opposite configuration to that which is obtained by means of the same reagent on the ester.

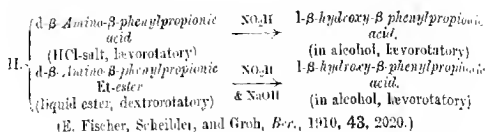
The question now arises as to whether in the case of the esters the transformation is accompanied by configurative change, and without configurative change in the case of the free acids, as postulated by Bühlmann, or vice versa.

There would appear to be no available data by means of which this question can be answered decisively. For the present therefore we have only the remarkable empirical regularity which is consistent with Bühlmann's hypothesis, but would, of course, be equally consistent with its opposite.

The Bühlmann hypothesis is, however, not borne out by the action of nitrous acid on the following amino-acids and their esters:



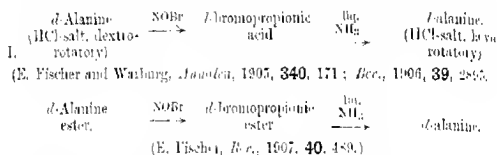
(E. Fischer and Weibhold, *Ber.*, 1908, **41**, 1293.)



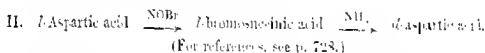
Thus, in the case of both these acids, the action of nitrous acid is the same on the ester as on the free acid itself. These are, however, the only cases in which the action of nitrous acid on an amino acid and its ester appear to have been investigated.

*In both of these acids the phenyl group is attached directly to the asymmetric carbon atom; these might, therefore, quite conceivably prove to be exceptional cases.*

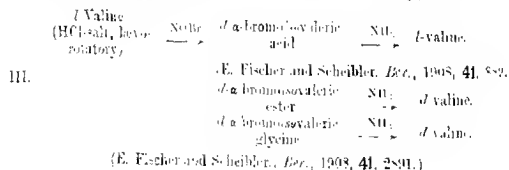
*Action of NH<sub>3</sub> on Halogen Acids and their Esters which have themselves been obtained from Amino-acids and Esters.*



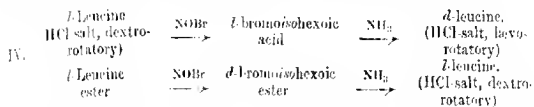
If the action of NOBr on the acid is normal, then the action of NH<sub>3</sub> on the bromo-acid is *abnormal*, whilst if the action of NOBr on the ester is abnormal, then the action of NH<sub>3</sub> on the bromo-ester is *abnormal* also, and there would be a double inversion in the passage from *d*-alanine ester to *d*-alanine. Moreover, whether the action of the NH<sub>3</sub> is normal or abnormal, it is the same in the case of the bromo-acid and its ester.



In this case, if NH<sub>3</sub> acts normally, then inversion must have taken place in the action of NOBr, which is contrary to the Bihmann hypothesis, but if NH<sub>3</sub> again acts *abnormally* in this case, then both I and II are consistent with the Bihmann hypothesis.



Thus the action of  $\text{NH}_3$  on the acid is the opposite of that on the ester and the glycine respectively. If the action of  $\text{NOBr}$  is normal, as it should be (Bilmmann), then that of the  $\text{NH}_3$  on the bromo-acid is *normal* also, and on the ester and glycine *abnormal*.

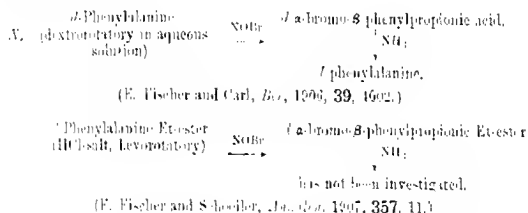


E. Fischer and Carl, *Ber.*, 1906, **39**, 3698; E. Fischer, *Ber.*, 1906, **39**, 2929;  
E. Fischer and Schoeller, *Annalen*, **357**, 13; E. Fischer, *Ber.*, 1901, **34**, 115;  
1907, **40**, 592.

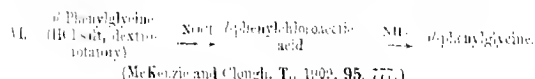
If the action of  $\text{NOBr}$  on the acid is normal, then the action of  $\text{NH}_3$  on the bromo-acid is abnormal, whilst if the action of  $\text{NOBr}$  on the ester is abnormal, then the action of  $\text{NH}_3$  on the bromo-ester is abnormal also.

Thus, in the case of alanine, leucine, and aspartic acid, the phenomena are consistent with the Bilmmann hypothesis, provided that the action of  $\text{NH}_3$  is abnormal.

Valine, however, differs from alanine and leucine, inasmuch as  $\text{NH}_3$  must be supposed to act normally on the free  $\alpha$ -bromoisovaleric acid, or, if the action of  $\text{NH}_3$  is abnormal, then the action of  $\text{NOBr}$  on valine is abnormal also, so that one or other of the steps is exceptional.



Thus, if the action of  $\text{NOBr}$  on *d*-phenylalanine is normal, as it should be (Bilmmann), then the action of  $\text{NH}_3$  is abnormal.



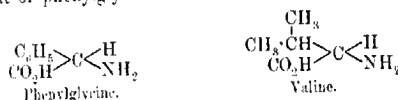
Thus, if the action of  $\text{NOCl}$  is normal, as it should be (Bilmmann), then the action of  $\text{NH}_3$  is normal also.

Thus, in the investigation of the behaviour of  $\text{NH}_3$  on the halogen acids, basing the configuration of the latter on the Bilmmann

hypothesis with regard to the normality of the action of NOBr and NOCl on the free amino-acids, we find that the action of  $\text{NH}_3$  is consistently abnormal, excepting in the case of the valine and phenylglycine series of transformations.

It will be seen later on (p. 734) that *L*-phenylchloroacetic acid (obtained from *D*-phenylglycine by the action of NOCl) forms an exception in its behaviour with KOH and  $\text{Ag}_2\text{O}$  respectively. On the other hand, it does not form an exception, as regards its formation from *D*-mandelic acid by the action of phosphorus pentachloride, in which, as usual, the change of sign, and as is therefore assumed, the change of configuration, takes place. I think, however, that it may fairly be argued that phenylglycine and its derivatives (phenylchloroacetic acid and mandelic acid) all possess a very exceptional constitution (the phenyl and carboxyl groups being directly attached to the asymmetric carbon atom), and that, therefore, exceptional behaviour should occasion the less surprise.

The constitution of valine is perhaps also, in certain respects, not unlike that of phenylglycine:



I may mention in this connexion that in all cases in which we have this same grouping of phenyl attached to the asymmetric carbon atom (irrespective of whether this is in the  $\alpha$ - or the  $\beta$ -position to the carboxyl group, if present), we have also a consistent behaviour of  $\text{SOCl}_2$  on the hydroxyl compound (no change of sign) (see p. 720).

The assumptions made in the above reactions lead to the further conclusion that:

<i>d</i> -Alanine (HCl-salt, dextrorotatory)	has the same configuration as <i>L</i> -bromopropionic acid.	
<i>L</i> -Leucine (HCl-salt, dextrorotatory)	"	<i>L</i> - $\alpha$ -bromoisobutyric acid
<i>L</i> -Aspartic acid (HCl-salt, dextrorotatory)	"	<i>L</i> -chlorosuccinic acid.
<i>L</i> -Valine (HCl salt, levorotatory)	"	<i>d</i> - $\alpha$ -bromoisobutyric acid.
<i>d</i> -Phenylalanine	"	<i>d</i> - $\alpha$ -bromo- $\beta$ -phenyl- propionic acid.
<i>d</i> - $\alpha$ -Amino- $\omega$ -chloro- $\alpha$ -phenylacetic acid	"	<i>L</i> - $\alpha$ -chloro- $\alpha$ -phenyl- propionic acid.
<i>d</i> -Glutamic acid	"	<i>L</i> - $\alpha$ -chloroglutaric acid.
<i>d</i> - $\beta$ -Aminobutyric acid	"	<i>L</i> - $\beta$ -chlorobutyric acid.
<i>d</i> -Phenylglycine	"	<i>L</i> -phenylchloroacetic acid.

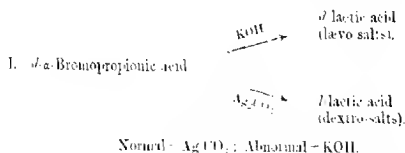
Further, if we assume the normal action of nitrous acid, then:

d- <i>Alanine</i> (HCl salt, dextrorotatory)	has the same configuration as d- <i>lactic acid</i> (levorotatory salts and esters).
d- <i>Serine</i> (HCl salt, levorotatory)	" " 1- <i>glyceric acid</i> (dextrorotatory salts and esters).
l- <i>Aspartic acid</i> (HCl salt, dextrorotatory)	" " 1- <i>malic acid</i> (levorotatory salts and esters).
l- <i>Valine</i> (HCl salt, levorotatory)	" " 1- <i>hydroxyisovaleric acid</i> (dextrorotatory salts).
d- <i>Phenylglycine</i> (HCl salt, dextrorotatory)	" " 1- <i>mandelic acid</i> .
d- $\beta$ - <i>aminobutyric acid</i>	" " 1- $\beta$ - <i>hydroxybutyric acid</i> .
l- $\beta$ - <i>Amino-<math>\beta</math>-phenylpropionic acid</i> (HCl salt, dextrorotatory)	" " d- $\beta$ - <i>hydroxy-<math>\beta</math>-phenylpropionic acid</i> (in alcohol, dextrorotatory).
d- <i>Glutamic acid</i>	" " 1- $\alpha$ - <i>hydroxyglutaric acid</i> (levorotatory salts).

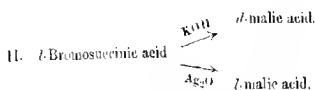
If we assume the above relationships between the configurations of the amino-acids and the halogen acids on the one hand, and between the amino-acids and the hydroxy-acids on the other, then we can draw the further conclusions that:

- I. 1-*Bromopropionic acid* has the same configuration as d-*lactic acid*  
(levorotatory salts and esters).
- II. 1-*Chlorosuccinic acid* " " 1-*malic acid*.
- III. d-*Bromoisovaleric acid* " " 1- $\alpha$ -*hydroxyisovaleric acid*  
(dextrorotatory salts).
- IV. 1-*Phenylchloroacetic acid* " " 1-*mandelic acid*.
- V. 1- $\alpha$ -*Chloroglutaric acid* " " 1- $\alpha$ -*hydroxyglutaric acid*.
- VI. 1- $\beta$ -*Chlorobutyric acid* " " 1- $\beta$ -*hydroxybutyric acid*  
(levorotatory ester).

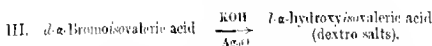
In the above pairs of acids, the identity of configuration is based on the assumption that the hydroxy-acid is formed from the amino-acid without change of configuration, and similarly that the formation of the halogen from the amino-acid proceeds without configurative change. Proceeding further, we can, with the aid of these assumptions, now test other configurative relationships. Thus, the different action of different bases, especially of alkalis and silver oxide respectively, can be investigated. Thus:



Note.— $\text{Ag}_2\text{O}$  acts oppositely on the bromo-acid and on its glycine.

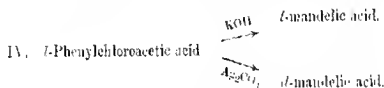


Normal =  $\text{Ag}_2\text{O}$ ; abnormal = KOH.

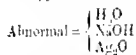
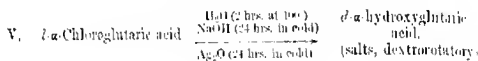


Normal =  $\text{Ag}_2\text{O}$  and KOH.

*Note.*— $\text{Ag}_2\text{O}$  acts in same way on the bromo acid and on its glycine.

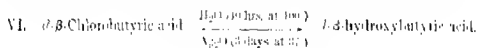


Normal = KOH; Abnormal =  $\text{Ag}_2\text{O}$ .



(E. Fischer and Moreschi, *Ber.*, 1912, **45**, 2447.)

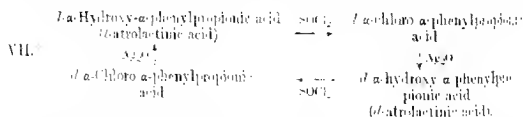
*Note.*—The quantity of  $\text{Ag}_2\text{O}$  added (1.5 grams to 0.5 acid) was only just sufficient to form the Ag-salt, which is insoluble. Therefore no evidence that Ag-ions had acted at all; may have been due to action of water alone. The polarimetric figures show that with NaOH, the reaction was complete in five hours in the cold.



(Fischer and Scheibler, *Ber.*, 1909, **42**, 1219.)

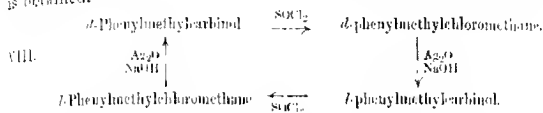
*Note.*—Even with  $\text{H}_2\text{O}$  and  $\text{Ag}_2\text{O}$  there is much racemisation, whilst NaOH and even  $\text{Na}_2\text{CO}_3$  cause complete racemisation. The Ag-salt is very insoluble; four times the calculated quantity of  $\text{Ag}_2\text{O}$  was employed in the hydrolysis.

The following two cycles of changes may also be included here:



\* In these cases the relative configurations of the hydroxy and halogen compounds can only be fixed by the relation of their rotation signs.

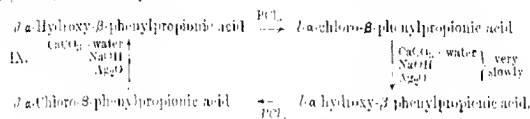
The results in the case of  $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid are particularly important, as the abnormal action of  $\text{Ag}_2\text{O}$  cannot be attributed to the action of water (OH-ions) predominating over the action of Ag-ions, because McKenzie and Clough (T., 1910, 97, 1017) have shown that, using water alone, complete racemisation occurs, and that it is only when  $\text{Ag}_2\text{O}$  is used that any active product is obtained.



(McKenzie and Clough, *Brit. Assoc. Reports*, 1912; this vol., p. 657.)

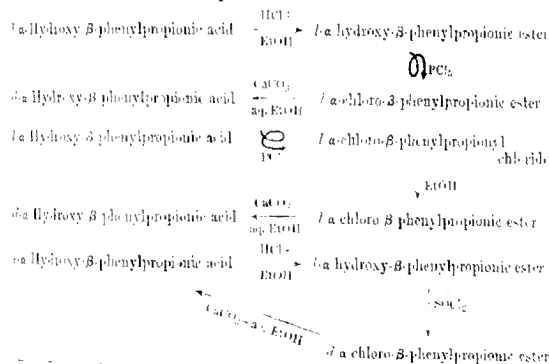
Inasmuch as in both these cases, VII and VIII,  $\text{SOCl}_2$  presumably acts normally (see p. 720), the action of  $\text{Ag}_2\text{O}$  and  $\text{NaOH}$  alike must be abnormal.

Again, the following cycle has been realised (McKenzie and Wren, T., 1910, 97, 1356):



Inasmuch as the  $\text{PCl}_5$  may be assumed to act abnormally, *all the hydrolysing agents appear to act normally.*

The following reactions are very interesting, and require special interpretation. I have indicated by the symbol  $\mathcal{S}$  where I assume an inversion takes place, thus:

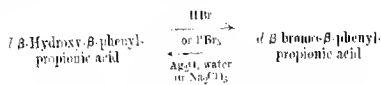


\* See footnote, p. 731.

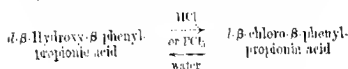


Thus, in all these cases, again the  $\text{CaCO}_3$  acts normally. This conclusion involves the  $\alpha$ -chloro- $\beta$ -phenylpropionic ester having the same configuration as the hydroxy-acid or ester of opposite sign, just in the same way as I have supposed that ethyl glycerate (lævo-rotation) has the opposite configuration to the levorotatory ethyl dichloropropionate (compare p. 718).

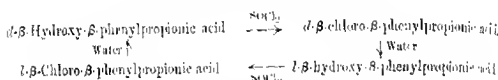
Again, the following may be considered:



(McKenzie and Humphries, T., 1910, 97, 121.)



(McKenzie and Barrow, T., 1911, 99, 1915.)



(McKenzie and Barrow, *loc. cit.*)

In these reactions, again, if  $\text{PCl}_5$  and  $\text{SOCl}_2$  be assumed to act abnormally and normally respectively, then the action of the water and other reagents would be uniformly abnormal (that is, causing a configurative change).

The whole of the hydrolysis results (10 cases) may be thus summarised:

*Sign Changes on Hydrolysis of Halogen Compounds.*

Change of sign = - . . . . . No change of sign = 0.

	KOH, etc	AgO
I. $\frac{1}{2}$ -Bromopropionic acid . . . . .	-	0
II. $\frac{1}{2}$ -Bromosuccinic acid . . . . .	+	0
III. $\frac{1}{2}$ -Bromosuccinic acid . . . . .	0	0
IV. $\frac{1}{2}$ -Phenylchloroacetic acid . . . . .	0	
V. $\frac{1}{2}$ -Chloroglutaric acid . . . . .	-	
VI. $\frac{1}{2}$ - $\beta$ -Chloropropionic acid . . . . .	- $\text{H}_2\text{O}$	+
VII. $\frac{1}{2}$ - $\alpha$ -Chloro- $\beta$ -phenylpropionic acid . . . . .	...	
VIII. $\frac{1}{2}$ -Phenylmethylchloromethane . . . . .	+	
IX. $\frac{1}{2}$ - $\alpha$ -Chloro- $\beta$ -phenylpropionic acid . . . . .	0	+
X. $\frac{1}{2}$ -Bromo- $\beta$ -phenylpropionic acid . . . . .	+	+

\* See footnote, p. 731.

† The configurative relationship between the hydroxy- and the halogen-compound can be tentatively fixed by the Büllmann hypotheses with regard to the action of  $\text{HNO}_2$  and  $\text{NOCl}(\text{NOBr})$ .

‡ The configurative relationship can be fixed by the tentative hypothesis with regard to the action of  $\text{PCl}_5$ ,  $\text{PIBr}_2$  on the hydroxy-compound.

In the first six of the above cases there are sufficient data to admit of the two Bihlmann hypotheses being tested. These hypotheses are:

(1)  $\text{NO}_2\text{H}$ ,  $\text{NOCl}$ , and  $\text{NOBr}$  act *normally* on the free amino-acids, and *abnormally* on their esters.

(2) When  $\text{KOH}$  and  $\text{Ag}_2\text{O}$  act oppositely on a halogen acid, the  $\text{Ag}_2\text{O}$  acts *normally*, and the  $\text{KOH}$  *abnormally*.

The two cases (I and II) above are entirely consistent with the Bihlmann hypotheses. In case III, the hypotheses are verified as regards  $\text{Ag}_2\text{O}$ , but not as regards  $\text{KOH}$ . In case IV, the results are the reverse of those which the hypotheses predict. In case V the result confirms the Bihlmann hypothesis as regards  $\text{NaOH}$ , but contradicts it as regards  $\text{Ag}_2\text{O}$ . There is, however, no evidence that in this case there was any Ag-ion present in the solution. In case VI it is also doubtful whether the Ag-ion was the active agent, as the Ag-salt is very insoluble, and the reaction was carried out in very dilute solution.

By means of the configurative relations given on p. 736, we can further test the action of  $\text{PCl}_5$ ,  $\text{PBr}_5$ , and  $\text{SOCl}_2$  on the hydroxy-acids. Thus:

I.	d-Lactic acid (levo-salts and e-ters)	$\xrightarrow[\text{PBr}_5]{\text{PCl}_5}$	d-chloro(bromo)propionic acid (change of configuration).
II.	l-Malic acid	$\xrightarrow[\text{SOCl}_2]{\text{PCl}_5}$	d-chloro-succinic acid (change of configuration).
III.	No data available.		
IV.	l-Mandelic acid	$\xrightarrow[\text{PBr}_5]{\text{KOH}}$	d-phenylchloroacetic acid d-phenylbromoacetic acid (change of configuration).
V.	No data.	$\xrightarrow[\text{SOCl}_2]{\text{NaOH}}$	l-phenylchloroacetic acid (configuration unchanged).
VI.	l-β-Hydroxyphenylacetic acid	$\xrightarrow{\text{PCl}_5}$	d-β-chloro-α-phenylacetic acid (change of configuration).

Thus, in all the four cases in which the data are available, the halogen compounds of phosphorus effect a change of sign, which, on the previous assumptions, betrays a change of configuration, whilst out of the two cases in which the data are available for  $\text{SOCl}_2$  in one there is change, and in the other no change of sign or configuration. It is very significant that the case in which the  $\text{SOCl}_2$  causes no sign change and, as is assumed, no change of configuration, is the only one in which phenyl is directly attached to the asymmetric carbon atom. A regularity in connexion with this structure has already been pointed out (see p. 732).

*Summary.*

As already pointed out, it would appear that there does not exist at the present time any criterion whereby the relation between the configuration of an optically active compound and that of a derivative from it can be decisively ascertained. Until the discovery of the Walden inversion it was always tacitly assumed that an optically active compound and a derivative prepared from it had the same configuration, excepting in so far as the preparation might be attended with racemisation phenomena (this statement is intended to include such cases as the preparation of *d*-gluconic acid from *d*-mannonic acid). The phenomenon of the Walden inversion shows, however, that we cannot admit such an assumption *prima facie* in the case of any derivative obtained by the substitution of a group attached to an asymmetric carbon atom.

In the absence of any criterion for definitely ascertaining configurative relationship, we naturally have recourse to hypotheses, and seek for cumulative evidence for or against them. Such hypotheses are likely to be based on (a) *whether the passage from one compound to another is or is not accompanied by a change of sign in the rotation*; (b) *whether the reaction which leads from one compound to the other is on general grounds likely or unlikely to be attended by a change of configuration*.

The hypotheses which I have endeavoured to investigate are:

(1) That the change of sign which almost invariably accompanies the action of  $\text{PCl}_5$  or  $\text{PBr}_5$ \* is, in the absence of evidence to the contrary, to be regarded as betraying a change of configuration. However, Pickard and Kenyon (T., 1911, **99**, 45; *B.c.*, 1912, **45**, 1592), as well as McKenzie and Humphries (T., 1910, **97**, 121) and McKenzie and Barrow (T., 1911, **99**, 1923), have also uniformly found a change of sign to occur when the halogen compound is prepared by means of halogen acid from the hydroxy-compound, so that the mechanism does not apparently depend on the phosphorus.

(2) That in those cases in which  $\text{SOCl}_2$  brings about a change of sign, there is also a change of configuration. And inasmuch as in all cases known in which  $\text{SOCl}_2$  does not bring about a change of sign, there is the uniform circumstance of a phenyl group being directly attached to the asymmetric carbon atom, it would appear that it is possible this circumstance which leads to an exceptional behaviour of  $\text{SOCl}_2$  in those cases. That the phenomena attending substitution at an asymmetric carbon to which a phenyl group is

\* For exceptions, see pp. 717, 718

directly attached are of an exceptional character is closely connected with the observations both of E. Fischer and of McKenzie, that this particular structure is especially liable to give rise to extensive racemisation during substitution.

(3) For reasons already indicated, Bühlmann has assumed the probability of there being no configurative change when  $\text{NO}_2\text{H}$ ,  $\text{NOCl}$ , or  $\text{NOBr}$  act on the free amino-acids, but that configurative change may take place when these reagents act on the esters of the amino-acids.

There does not appear to be any experimental evidence that  $\text{NO}_2\text{H}$  acts oppositely on amino-acids and on their esters respectively; in the only two cases investigated, on the contrary, the action is the same on both.

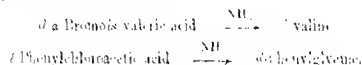
On the other hand, in the only four cases in which the action of  $\text{NOCl}$  or  $\text{NOBr}$  has been investigated both on a free amino-acid and on its ester, the action on the two is opposite.

By means of these assumptions we may tentatively fix the configurative relations between a number of amino-acids and their hydroxy- and halogen derivatives respectively. Thus data are available for tentatively fixing this relation between 9 amino-acids and 9 halogen acids, and between 8 amino-acids and 8 hydroxy-acids respectively.

(4) Having fixed these configurative relations, I have proceeded to investigate from this basis the several reactions in which a halogen is replaced by the  $\text{NH}_2$ -group.

Data are available for the investigation of six cases of such substitution (see pp. 730, 731).

In four out of these six cases the action of  $\text{NH}_3$  proves to be *abnormal*, that is, the substitution of halogen by  $\text{NH}_2$  is attended with configurative change. The two other cases, which may be called exceptional, are those of:



We may therefore perhaps tentatively conclude that the usual course of the substitution of a halogen by  $\text{NH}_2$  is *abnormal* (that is, attended by configurative change) on the assumptions made in this investigation.

(5) Again starting from the configurative relations referred to in paragraph (3), I have investigated the several reactions in which a halogen is replaced by the  $\text{OH}$ -group. These are the reactions which have given rise to the recent suggestive speculations of Gadamer and of Bühlmann, as well as to the interesting investigations of Senter.

Data are available in ten cases, but in several the data are unfortunately somewhat fragmentary, and the necessarily different conditions under which the hydroxylation takes place militate against the utility of the results for purposes of comparison.

In three out of the ten cases a different product is obtained, according as the hydroxylation is effected with  $\text{Ag}_2\text{O}$  or with  $\text{KOH}$  respectively, and in two\* of these three cases  $\text{Ag}_2\text{O}$  acts *normally* and  $\text{KOH}$  *abnormally*, in accordance with the Büllmann hypothesis, whilst in the third † case it is  $\text{KOH}$  which acts *normally* and  $\text{Ag}_2\text{O}$  *abnormally*.

In two cases ( $\alpha$ -bromoisovaleric and  $\alpha$ -chloro- $\beta$ -phenylpropionic acids), both  $\text{Ag}_2\text{O}$  and  $\text{KOH}$  act *normally*, whilst again, in the five remaining ‡ cases, all the hydrolysing agents act *abnormally*, that is, produce a configurative change.

It is evident therefore that just in the replacement of halogen by hydroxyl there is apparently great irregularity, and hence most difficulty in harmonising the results with the demands made by the speculations of either Büllmann ( $\text{Ag}_2\text{O}$  normal,  $\text{KOH}$  abnormal) or Gadamer ( $\text{Ag}_2\text{O}$  abnormal,  $\text{KOH}$  normal) respectively.

It is obvious that there are many complicating factors in these transformations; for example, the insolubility of the silver salt, and the consequent uncertainty of whether there is an effective concentration of Ag ions present. In my previous presidential address (T., 1912, 101, 683), I called attention to the contradictory results which had been obtained in the relative facility with which  $\text{AgBr}$  separates from silver bromofumarate and bromomalate respectively according to the conditions of experiment, and it is probable that similar complicating factors come into play in the reactions under discussion now.

The complexity of the reactions in which the halogen of halogen acids is replaced by hydroxyl is strikingly brought out by the extended investigations of Senter, in which some most unexpected phenomena have been brought to light. It is therefore not surprising that the configurative relations connected with these reactions should at present be so obscure.

There is one regularity in the hydroxylation results which is perhaps worthy of attention, and that is that in the only three cases investigated of compounds having a phenyl group directly attached to the asymmetric carbon atom, the action of silver oxide is abnormal (that is, attended with configurative change) according

\* Bromoisovaleric acid and bromosuccinic acid.

† Phenylchloroacetic acid.

‡  $\alpha$ -Chloroglutaric acid,  $\beta$ -chlorobutyric acid,  $\alpha$ -chloro- $\alpha$ -phenylpropionic acid, phenylmethylchloroacetone, and  $\beta$ -bromo- $\beta$ -phenylpropionic acid.

to the configurative relations which I have deduced from the assumptions made.

I would suggest that several distinct processes of hydroxylation, according to the conditions employed, should be recognised:

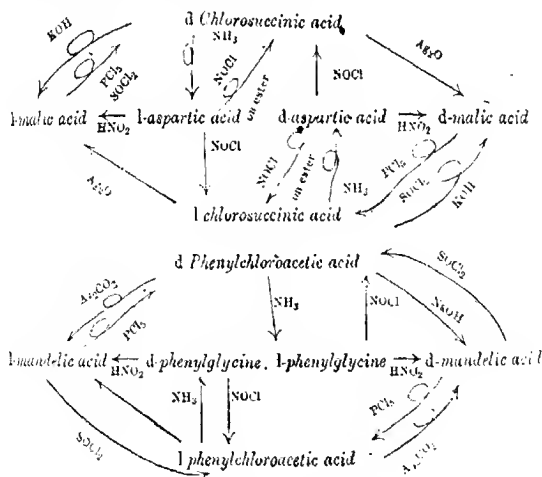
(1) The silver salt may in the first instance split off silver haloid *internally*, the hydroxyl ion of the water becoming simultaneously attached.

(2) The halogen may be removed by silver-ion, forming insoluble and non-ionised silver haloid, the hydroxyl-ion of the water becoming simultaneously attached.

(3) The halogen may be similarly removed by cations, forming soluble but non-ionised haloids (mercury, palladium, etc.).

(4) The halogen may become ionised and remain ionised in the form of halogen acid (when water acts alone) or as ionised haloids (when potash, soda, lime, etc., are used in the hydrolysis).

The following diagram, showing the transformations which have been effected in the case of malic and mandelic acids respectively, will perhaps best illustrate the configurative relations which have been developed in the present discussion. In this diagram the symbol  $\rightarrow$  indicates a transformation *without*, and  $\odot$  a transformation *with configurative change*.



It must be clearly understood that the foregoing investigation, made of the available data, only displays the relative effects of the

several reagents employed, and that these *relations* would be equally true if the terms *normal* and *abnormal* were employed in the opposite sense to that in which I have used them throughout, for we have at present, as I have so often reiterated, no criterion whereby the occurrence or non-occurrence of a configurative change in a process of substitution can be decisively tested.

It is evident that a very large amount of experimental work has still to be carried out before the numerous complex and highly important issues arising out of the phenomenon of the Walden inversion can be fully elucidated. I trust that the account which I have endeavoured to give of the present position of the subject may serve to indicate the various directions in which the inquiry can be advantageously prosecuted.

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## OBITUARY NOTICES.

### PAUL ÉMILE (DIT FRANÇOIS) LECOQ DE BOISBAUDRAN.

BORN 1838; DIED MAY 28TH, 1912.

FRANÇOIS LECOQ DE BOISBAUDRAN belonged to the ancient Protestant nobility of Poitou and Angoumois; they were people of considerable fortune, which, however, the revocation of the Edict of Nantes caused to disappear. The property of Boisbaudran was sold; and his father Paul, together with his brother Scævola, an old student of the École Polytechnique, started a wine business at Cognac. At first, the venture was not very successful; but as time went on things prospered, and young Lecoq entered the business, for it needed all the energy of the family to keep things going. Lecoq was blessed with an excellent mother; she was the daughter of an officer, and was exceptionally gifted; from her, her son learned the classics, history, and foreign languages. The writer made his acquaintance in the late '60's, when he visited Glasgow, "travelling in wine," and he spoke English fluently and with little accent, although he had not quite mastered the niceties of the language: on one occasion he astonished an elderly lady, his partner at dinner, by the remark, "Madam, the soup is devilish hot."

During the intervals of his travels he spent his small leisure in

working through the courses of the *École Polytechnique*, of which he had procured the syllabus. He thus acquired a very general knowledge of science; but the problems of chemistry and physics were those which most attracted him; and he fitted up a modest laboratory, where he began to repeat the experiments and methods of analysis of which he had read in books. In this he was helped by the liberality of one of his uncles. It was in this laboratory that he made most of his early discoveries; it was there that gallium was first isolated. He met with encouragement from all members of his family. It was one in which old Protestant principles, fortified by persecution, survived; and its watchwords were justice, kindness, and the sense of personal responsibility; in such a family François Lecoq received his training.

De Boisbaudran's early work had reference to the phenomena of supersaturation of solutions. It was he who first showed that supersaturation is destroyed by contact with crystals of an isomorphous salt, and also that it is possible to prepare solutions of anhydrous salts in a supersaturated condition (1866 to 1869). Incidentally, he pointed out the presence of isodimorphism in double sulphates. In 1874 he published the interesting fact that octahedral faces are less readily soluble than cubical faces in the case of ammonium alum. In 1871 he was in advance of his time in suggesting devices for the electric deposition of metals for analytical purposes. His chief work, however, may be treated under three heads: (1) his spectroscopic studies; (2) their application to the discovery of gallium; (3) their application to his researches on the rare earths.

In 1865 Lecoq deposited a "*pli cacheté*" with the Academy of Sciences, which was opened by his request in 1871; he summarised its contents as follows: "It is well known that molecules the vibrations of which produce light have isochronous periods of oscillation, for they give rise to rays of determinate wave-length, constant for each substance. The force which tends to bring back the molecule to its centre of oscillation is the reaction of the ether on the molecule; this reaction remains constant so long as the mass and the velocity of the molecule do not change, but varies when the relative masses of the ether and the molecule vary. A heavier molecule therefore returns to its centre of equilibrium with less energy than a lighter, and consequently takes a longer time to oscillate through this point; its wave-length is greater. It is the vibration of the whole molecule which produces light; when a compound resists a high temperature without decomposing, its spectrum is different from that of its elements. In such a case, as in that of elements, the less refrangible rays are due to the



heavier compound, when the compounds have the same chemical constitution." These ideas led him to the following conclusions.

"(1) The lines of a spectrum are derived from one or more primitive lines, which form an elementary group; this, by successive increases or diminutions of the wave-length, repeats itself in the spectrum without altering the general appearance.

"(2) For the same natural family, the mean wave-length of the elementary groups is a function of the respective atomic weights; the general form of the spectrum therefore persists on passing from one element of the same chemical type to another; the only change it undergoes is that due to the change of mass of the molecules.

"(3) In a series of analogous spectra, the mean wave-lengths of the harmonics are greater the higher the atomic or molecular weights of the elements or compounds which give the spectra."

In order to collect material for testing these generalisations, Lecoq made an elaborate study of the spectra of thirty-five elements, in some cases using the Bunsen burner to cause luminescence, in others an electric spark, and in others both. The results of these laborious investigations were published in 1874 in a handsome volume entitled "*Spectres Lumineux*." In observing spark spectra, he made use of a solution of a salt of the element to be examined, contained in a glass tube, through the bottom of which a platinum wire was sealed; this was made the negative pole; the positive was a stouter piece of platinum wire, a few millimetres above the surface of the liquid. In 1885, by reversing the current and making the liquid positive, he obtained phosphorescent bands instead of a line spectrum; by aid of this arrangement, he succeeded in discovering three new metals, to which he gave the provisional names  $Z\alpha$ ,  $Z\beta$ , and  $Z\gamma$ ; these have since been named dysprosium, terbium, and europium. He also produced phosphorescent spectra by directing the negative stream on to the substance in powder, placed in a vacuum; and, as early as 1866, he introduced the idea of solid solutions to chemistry. His view was that the spectrum is due to the dissolved substance, and he carried out many researches in reference to the subject. His conclusions differed, it may be remembered, from those of Sir William Crookes; an excellent summary of the controversy is to be found in the *Annales de Chimie et de Physique* for 1909, by M. Urbain.

Lecoq de Boisbandran first attracted the universal attention of chemists by his discovery of gallium. In February, 1874, he began the investigation of 52 kilograms of blende from Pierrefitte (Hautes-Pyrénées). The solution of this mineral gave a deposit on metallic zinc which revealed in the spectroscope a hitherto unknown line of wave-length 4170; further research revealed another line at

wave-length 4031. These two lines are not shown in the Bunsen flame, but they appear by aid of an oxy-hydrogen flame; Sir W. N. Hartley has recognised the wide distribution of gallium by their aid. In 1875 he had obtained several milligrams of gallium chloride; and he transferred his materials to Wurtz's laboratory in Paris, where he demonstrated the reality of his discovery. His experiments were recommenced with several hundred kilograms of blende, and in the same year he succeeded in preparing the metal by electrolysis a solution of the hydroxide in potassium hydroxide; he obtained more than a gram of metal. Later on, in collaboration with Jungfleisch, he obtained 75 grams of metal from over 4000 kilos. of blende. The extraction was carried out in the factory at Javel.

From his generalisation (2), already quoted on p. 744, he calculated the atomic weight of gallium as 69.86; the mean of two sets of determinations gave the same figure. He also calculated the atomic weight from a periodic arrangement of the elements, which, although not published until 1895, was constantly discussed in the early '60's with Dumas and Friedel. It does not differ in any marked particular from those generally accepted.

One of the fruits of this magnificent work was the bestowal on him of the Cross of the "Legion d'Honneur"; he succeeded Malaguti as Correspondent of the Institute in 1878; he was awarded the Davy Medal in 1879; and the Prix Lacaze of 10,000 francs. He was elected a Foreign Member of our Society in 1888.

It was in 1869 that he began his work on rare earths; his familiarity with spectroscopic methods peculiarly fitted him for this task. In that year Lecoq showed that the didymium from cerite differed from that of samarskite; he had as a collaborator the American, Lawrence Smith. In July of that year he announced the discovery of samarium, defined by its absorption bands. Marignac separated the same element later, and characterised it by the letter Y. From Marignac, Lecoq obtained a specimen of earth separated during the fractionation which yielded samarium, and in it he detected a new element, subsequently named gadolinium. In 1904 he gave the provisional letter Z to the element contained in an earth separated from impure terbia, and this has been identified by Urbain as pure terbia.

In studying the spectra of solutions, in which the liquid was made the positive pole, Lecoq noticed a citron band as well as a green one in fractions of the rare earths precipitated by potassium sulphate. In 1886 he succeeded in obtaining the earth yielding the citron band in a pure state; and he named it dysprosium, a word meaning "difficult to obtain."

After 1895, family duties and failing health hindered his work. Along with M. le Comte de Gramont (to whose excellent article in the "Revue Scientifique" the writer is chiefly indebted for the facts of this notice), the spectrum of glucinum (beryllium) was studied; an account of his experiments was published in 1911. M. le Comte de Gramont is issuing a further volume on spectra, of which the work was carried out by Lecoq in his later years.

Lecoq de Boisbandran married late in life, and his marriage brought him much happiness. His sufferings from ankylosis of the joints, which were very severe, were borne with stoical resignation. He passed away on May 28th, 1912, at the age of seventy-four.

W. RAMSAY.

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### EDWARD DIVERS.

BORN NOVEMBER 27TH, 1837; DIED APRIL 8TH, 1912.

#### I.

EDWARD DIVERS was born in London of Kentish ancestry November 27th, 1837. He had one brother, who was connected with the Thames Ironworks, and a sister. His sister, who survives him, is the widow of James O'Kinealy, a distinguished Colonial Judge, who had been a fellow student of Divers in Queen's College, Galway. In infancy Divers had an attack of inflammation of the eyes, which seriously impaired his vision, a defect which could not be remedied by glasses. Later in life, in 1884, an unfortunate explosion during an experiment so much aggravated this that he practically lost the use of his right eye. This defect of vision was a serious handicap to him throughout his life, and it is marvellous how notwithstanding he was able to conduct researches, as he did, involving the closest observational powers.

In 1850, at the age of thirteen, Divers entered the City of London School, one year after Perkin, where he came under the influence of one of the masters, Thomas Hall, who had been a student of Hofmann's at the Royal College of Chemistry, and who had become inspired by him as Divers himself and Perkin and so many others subsequently were. Hall gave experimental lectures in chemistry between class hours; there was no compulsion, no inducement, but simply the attraction of science and its boundless possibilities, both of its own advancement and of its applications

to the welfare and happiness of mankind. By this natural and efficient process the fittest were attracted, and from Hall the way was opened to Hofmann and the Royal College for many who are now well known in the annals of science. We are indebted to Perkin and to Divers himself for an account of Hall and what he did for chemistry in such a quiet, unobtrusive manner (T., 1896, 69, 599; Perkin Jubilee volume, 21).

This, the early years of the Royal College of Chemistry, is a period upon which chemists love to linger. The remarkable achievements going on around us to-day show that the boundaries of the unknown have not yet been reached, still there was a fruitfulness attending the work of the young Hofmann and his devoted followers, in Hanover Square, in Oxford Street, and in Jermyn Street, that arrests attention. Later, in the autumn of the life of that great leader, he told the writer that, at the time referred to, no matter what they touched, where they addressed their questionings to Nature, she seemed to respond willingly, disclosing important and suggestive results. With such a leader in research, with such a teacher, in the right meaning of the word, no wonder that those who came within his influence became inquirers and teachers too; and as he carried on the work of Liebig, so they carried on that of Hofmann. It was destined that Divers should carry it to Japan.

Divers was only one year at the College of Chemistry, the session 1852-3. This was the last session at the Oxford Street laboratories, the college being merged in the Jermyn Street School of Mines in 1853-4. Mr., now Sir William, Crookes was then assistant, and Divers ascribed much of the value of his training to the help which Mr. Crookes gave him. In 1853-4 Divers became a junior assistant in Stenhouse's laboratory in St. Bartholomew's Hospital Medical School, where Abel was then assistant, and both Kekulé and H. Buff were working. Stenhouse regarded Divers's defective vision too serious a hindrance to admit of the attainment of success in a chemistry career; but it is interesting to know that he was led afterwards to modify this opinion.

One of the effects of the movement associated with the arrival in this country of the Prince Consort, which gave rise to the Royal College of Chemistry, was the foundation in Ireland of the Queen's University, with its federated colleges in Belfast, Cork, and Galway. It was natural, therefore, that the chemistry chairs in those colleges should be intimately related to the College of Chemistry. Thus Blyth, Hofmann's assistant professor, was one of the first professors at Cork, and Rowney, an assistant of Hofmann's, became a professor at Galway, succeeding Liebig's student, Ronalds. Ronalds in 1854 required an assistant, and Divers accepted the position, and con-

tinued in the same capacity under Rowney, who became professor in 1856.

Divers went to Galway with the object of taking the University degree in medicine, one of the few scientific degrees then available, and at the same time to take advantage of the opportunities there afforded for teaching and research in chemistry. He remained there constantly until the completion of his medical curriculum, when he obtained the degree of M.D. in 1860, and afterwards, during the winter sessions until 1866, when he finally left Ireland and took up his abode in London, at Notting Hill. As assistant and demonstrator of chemistry in Galway for about twelve years, Divers was well known to the students, whom he attracted by his natural gifts as a teacher, and the late Prof. Allman, a well-known mathematician, often told the writer how he was himself attracted to Divers, and sought from him instruction in chemistry.

His medical experience was made use of in Galway as physician for a time to the fever hospital and in other minor appointments, and as a teacher of chemistry he was asked by the Committee of Council on Education to deliver popular lectures in Ballina and other places. After 1860, and until his Japanese appointment in 1873, he also held various teaching appointments in England, as Lecturer in *Materia Medica* at Queen's College, Birmingham, and, in London, as Lecturer in Medical Jurisprudence at Middlesex Hospital Medical School, and in Physics at Charing Cross Hospital Medical School. He was also Lecturer in Chemistry at the Albert Veterinary College, and contributed special reports from time to time to the medical journals on the quality of the London milk supply and other subjects.

Divers joined the Chemical Society in 1860, and in 1862 commenced the publication of the results of his experimental inquiries. His first paper is an account of a careful study of magnesium ammonium carbonate, which was followed in 1868 by one on zinc ammonium chloride, and in 1870 by three papers describing his classical investigation of the carbonates and carbamate of ammonium. He had studied in 1863 the spontaneous change which gun cotton undergoes with formation of gelatinous acids, and then in 1871 appear two papers in which he begins the study of nitrites, and announces his discovery of hyponitrites, the study of which he afterwards made so much his own. Another very interesting subject was investigated in 1873 just before his Japanese appointment, the interaction of ammonia and ammonium nitrate. The work recorded in these papers is a fitting introduction to the more important results of his activity in Japan: it is characterised by

accuracy even in the minutest detail and a keenness of observation all the more remarkable considering how much he was handicapped by his difficulty of sight.

In 1899, shortly after the death of his wife, Divers gave up his home in Japan and returned to this country. His interest in chemistry continued unabated, and especially in respect to those subjects upon which he had worked himself. But he will be remembered best as the centre of groups of younger workers, women as well as men, who looked to him as a leader, an old warrior, whom they delighted to honour. To them, particularly, he responded wholeheartedly, with a sympathy and affection they will not soon forget. His old University in Ireland, represented in 1897 by the Royal University, conferred on him its D.Sc. *honoris causa*, and the various societies in England and the British Association were glad to recognise his worth. He was President of Section B of the British Association (1902); Vice-President of the Chemical Society (1900-02); Vice-President of the Institute of Chemistry (1905), and the same year President of the Society of Chemical Industry. He was elected a Fellow of the Royal Society while in Japan, 1885.

A. S.

## II.

### *Dr. Divers's Life and Work in Japan.*

Dr. Divers came out to Japan in July, 1873. This country had then only begun to remodel its civilisation by systematically introducing Western sciences and institutions, and several seats of liberal and technical education, based on the Western systems, were being established in Tokyo. The Engineering College at Toranomon was one of these, and it was here that Dr. Divers was asked to teach General and Applied Chemistry, this institution being fortunate in obtaining, from the earliest period of its existence, the services of such able men of science as the late Prof. Ayrton, Profs. Milne and Perry, besides Dr. Divers. Dr. Henry Dyer, of Glasgow, was the Principal of the College, and, on his resignation in 1882, Dr. Divers was asked to occupy the post thus left vacant, besides holding the Professorship of Chemistry.

In 1886 the Engineering College was incorporated with the Tokyo University, in which the several departments of Law, Literature, Science, and Medicine had already been established, and from that time Dr. Divers's service was transferred to the College of Science of the newly reorganised Imperial University of Tokyo.

where he held the Chair of Inorganic Chemistry until his return to England in 1899.

Coming out to Japan at the age of thirty-six and staying for twenty-six years, which were equally divided between the old Engineering College and the present College of Science, Divers spent the best part of his life in this country, and by his teaching and example during this long and meritorious service he greatly promoted the development of chemical science in Japan, besides contributing very largely to the general progress of chemistry.

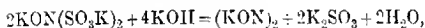
It is true that during his first seven or eight years in Japan Divers did not publish anything, but this was only because his time was too much taken up with other matters to devote his attention to original work. Not only were his professorial duties very heavy during this period, but he was also being constantly asked by the Department of Public Works, to which the Engineering College at first belonged, to undertake the analysis of minerals, valuations of ores, assay of gold and silver, and so forth, besides being occasionally consulted on questions connected with the chemical industry of the country.

The first papers published by Divers after coming out to this country were, indeed, those bearing on Japanese minerals, and these were communicated to the meetings of the British Association held in York in 1881. In one of these papers he described his observations on the occurrence of selenium and tellurium in Japanese sulphur, and he subsequently obtained a quantity of these elements from the lead-chamber deposits of the Osaka sulphuric acid work. The material thus obtained enabled him, with the assistance of Shimadé, who greatly distinguished himself afterwards as the discoverer of a powerful explosive, to do some good work on these elements, among which reference may be made to the discovery of a new oxide of tellurium, of tellurium sulphoxide, and of a new and simple method for the quantitative separation of tellurium from selenium. These and other papers on tellurium and selenium were published in the *Journal of the Chemical Society* during the years 1883-1885.

Divers's activity as an investigator became suddenly and particularly prominent about this time, for although his energy never seemed to be appreciably diminished except for the last year or two of his residence in this country, he published no less than twenty-four papers within the two years 1884-1885 in the *Journal of the Chemical Society* alone, and with the exception of those on tellurium and selenium, together with two or three minor communications, all these papers and also others subsequently published by him refer to the chemistry of nitrogen and sulphur compounds, to which

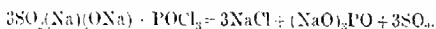
subject, indeed, few chemists have probably contributed more than he. It is quite impossible in this short notice to give anything like a brief summary even of the immense amount of work done by Dr. Divers in this particular field; only a few of the more important points brought to light by his work can therefore be offered for review.

Two years before coming out to Japan Dr. Divers published a very interesting and important paper on "The existence and Formation of Salts of Nitrous Oxide" (T., 1871, **24**, 484), and, taking up this work on hyponitrites again in 1884, he, in collaboration with Haga (T., 1884, **45**, 78), established the composition of silver hyponitrite to be  $(\text{AgNO})_2$  against the formula  $\text{Ag}_2\text{N}_2\text{O}_4$  asserted to be true by Berthelot and Ogier. Several new modes of formation of hyponitrites were discovered at the same time, among which the ready decomposition of an oxyamidodisulphonate by an excess of strong alkali into a hyponitrite and a sulphite (T., 1889, **55**, 760) according to the equation:



is interesting as affording a proof that in hyponitrites the metallic radicle is not in direct union with nitrogen, but is united to it through oxygen. The reaction is also important as being suitable for preparing large quantities of hyponitrites, Kirschner's method of preparation being, in fact, based on this reaction.

In the paper entitled "On the constitution of some non-saturated oxygenous salts, and the reaction of phosphorus oxychloride with sulphites and nitrites" (T., 1885, **47**, 265), Divers brought forward strong reasons in favour of the sulphonic or unsymmetrical constitution of inorganic sulphites, and one of these was the very conclusive fact experimentally established by him that, by the action of phosphorus oxychloride on sodium sulphite, one-half of the sodium contained in the latter goes to form sodium chloride, whilst the other half is converted into sodium phosphate. Thus:



At the same time, he showed that Carins's work, according to which thionyl chloride formed by the action of phosphorus pentachloride on inorganic sulphites was regarded as a direct product of the reaction and which formed the only experimental evidence in favour of the symmetrical constitution of the sulphites, had no significance whatever, inasmuch as thionyl chloride was doubtless produced by a secondary reaction between sulphur dioxide and phosphorus pentachloride. It was in the course of the work now under review, and, in fact, on November 24th, 1884, that Divers had



a very serious accident, which cost him the loss of the sight of his right eye, it having been very badly cut by pieces of glass resulting from the sudden bursting of the bottle in which phosphorus oxychloride had been kept (compare *Chem. News*, 1885, **51**, 23).

In continuation of his work on the constitution of sulphites, Divers, in collaboration with Shimidzu, thoroughly investigated the very varied and numerous sulphites of mercury (T., 1886, **49**, 533), and brought to light many interesting peculiarities in the chemistry of this metal.

Fulminic acid and hydroxylamine also attracted a good deal of Divers's attention. Among other things, he and Kawakita proved, in a paper on "The constitution of the Fulminates" (T., 1881, **45**, 13), that formic acid formed a very important part of the products of decomposition of mercury fulminate by hydrochloric acid, a fact which had been quite overlooked by previous workers, who could not make out what the carbon of the fulminates became by this decomposition, whilst in the study of the formation of hydroxylamine from nitric acid (T., 1883, **43**, 413), it was shown that, of all the common metals, zinc or tin is best suited for effecting the reduction, and, further, in collaboration with Shimidzu (T., 1885, **47**, 597), that the presence of sulphuric or hydrochloric acid is essential for the production of large quantities of hydroxylamine, the non-addition of one of these acids yielding practically no hydroxylamine, but giving rise to the formation of ammonia and other products of reduction.

Of all subjects, however, the one which was most fully studied by Divers and which was made peculiarly his own was the chemistry of sulphonated nitrogen compounds. In collaboration with Haga, he showed that the numerous complex acids belonging to this group of compounds are the products of the reaction between sulphurous and nitrous acids, the base being essential only in so far as it protects the products of the reaction against hydrolysis, and that, contrary to the statements of previous workers, normal sulphites and nitrites have no action whatever on each other (T., 1900, **77**, 673). They further showed that the primary product of the reaction between sulphurous and nitrous acids is always dihydroxylaminedisulphonic acid and nothing else, no derivative of dihydroxylamine or of any quinquivalent nitrogen being ever formed. All the substances supposed by others to be such were proved to be merely double salts of hydroxylaminedisulphonate and alkalin nitrite, with or without alkali replacing the hydroxyl-hydrogen of the disulphonate, and to be synthetically obtainable from hydroxylaminedisulphonate, alkali nitrite, and alkali hydroxide

(T., 1900, 77, 432). The chemistry of these rather complex compounds was thus considerably simplified.

Divers was pre-eminently an experimental chemist. He was always busily engaged in an experimental work of some sort, but rarely occupied with the theoretical study of chemical questions, and this aptitude of his mind is doubtless to be traced to the influence and teaching which he early received from A. W. Hofmann at the Royal College of Chemistry, and to which he often used to refer in his conversation. Divers, in his turn, also greatly encouraged the spirit of experimental research, and in this he was most successful, for besides those of his old pupils already named as his collaborators, who are also well known as independent investigators, several others have distinguished themselves by publishing important experimental work, of whom mention may be made of Dr. J. Takaminé, of New York, who prepared pure adrenaline for the first time, and Prof. M. Ogawa, of the Tohoku Imperial University, who discovered the new element nipponium. Reference may perhaps be made here to the work of Prof. M. Chikashigé, of the Kyoto Imperial University, who is also an old pupil of Divers, and who, according to his suggestion, determined the atomic weight of Japanese tellurium (T., 1896, 69, 881), in the hope that this tellurium, which is associated with sulphur and not with any heavy metal, as is the case with European tellurium, might yield an atomic weight in conformity with the Periodic Law. The expectation, however, was not realised, the number obtained for the atomic weight of tellurium being 127.59, in close agreement with the values obtained in Europe.

In the lecture room, too, Divers always tried to avoid the use of hypothesis as much as possible, his Presidential Address on "Atomic Theory without Hypothesis," given to the Chemical Section of the British Association at its Belfast meeting in 1902, being a very interesting and faithful reflection of his mental attitude as a teacher. There was one theoretical question, however, which he used to discuss with much animation, and that was the theory of valency. The valency of an atom, according to Dr. Divers, represents the number of chemical reactions by which that atom parts with another atom or radicle united to it, and although in the case of a multivalent atom the second and succeeding steps often begin before the first is completed, thus giving rise to a mixture of products, each of the steps can, in some cases, be neatly followed, and the corresponding product easily isolated in a pure state. Thus, in the hydrolysis of nitrotrinitrisulphonic acid, the sulphonic groups are replaced by

hydrogen one after another, and each of the three products, namely, imidosulphonic acid, amidosulphonic acid, and ammonia, can be successively obtained unmixed with any of the other two.

Divers had two great misfortunes while in this country, and each of these gave him a very severe blow. The one was the sudden death of his son Frederic, which occurred in China, where he was in the service of the Maritime Customs under the late Sir Robert Hart, and the other was the loss of his beloved wife, Margaret Theresa, who died in Tokyo in 1897. After this, Divers never seemed to be in the best of spirits, and this fact, combined with his advancing age and isolation, led him ultimately to return to England in 1899. He was a most painstaking worker in whatever capacity his service was asked, and by his zeal and earnestness in the work he undertook, as well as by his straightforwardness, simplicity, and kindness, he won the respect and admiration of all who knew him well, among whom mention may be made of the late Prince Ito, who, in the early days of the old Engineering College, was the Minister of Public Works, and thus came in frequent contact with him.

The importance of Divers's service to the cause of education and learning in this country was early recognised by the Japanese Government, which, in 1886, conferred upon him the Order of Rising Sun of the Third Class, and again, in 1898, the Order of Sacred Treasure of the Second Class. In England, the Royal Society of London elected him a Fellow in 1885, in recognition of his important contributions to the general progress of chemistry, whilst in 1897 the Royal University of Ireland conferred upon him the honorary degree of Doctor of Science. He was further an Honorary Member of the Tokyo Chemical Society, the Society of Chemical Industry of Japan, and the Engineering Society, the last of which was established by those who were all Divers's students in the old Engineering College, and on his leaving Japan in 1899 the Imperial University of Tokyo conferred upon him the title of Emeritus Professor. In addition to these honours, a memorial bust of Dr. Divers was presented to the University by his old friends and pupils to be erected in the University grounds, and it was unveiled with due ceremony on November 17th, 1900 (compare *Chem. News*, 1900, 82, 310).

On receiving the painful news of the death of Dr. Divers, the Imperial University at once sent a telegram of sympathy and condolence to his relatives, and a month after this, on May 10th, 1902, a meeting of his old friends and pupils was held in one of the halls of the University in his memory, when Prof. Haga, who is Dr. Divers's successor in the University, gave a memorial lecture

compare *Chem. News*, 1912, 105, 275), which was afterwards printed in the *Journal* of the Tokyo Chemical Society.

Dr. Divers leaves behind him two daughters, both of whom were married in Japan, the elder, Edith, being married to Count Labry, who was a military attaché to the French Legation in Tokyo, and the younger, Ella, to Mr. E. W. Tilden, who was a resident of Kobe.

JOHN SARCEAL.

### HUMPHREY OWEN JONES, F.R.S.

BORN FEBRUARY 20TH, 1878; DIED AUGUST 15TH, 1912.

H. O. JONES was born at Goginan, in Cardiganshire, and came of that Welsh race which has given to Wales many of her most gifted and vigorous sons; this stock, which forms no inconsiderable part of the population in the district around his birthplace, has a strong Norse element blended with the earlier race. Up to seven years of age Welsh was his only speech. He first learnt English when his family removed their business to Ebbw Vale. Educated at Lewis's School, Pengam, he entered the University College of Wales, Aberystwyth, with a scholarship in 1894, and graduated as Bachelor of Science in the newly constituted University of Wales at its first congregation in 1897. In the same year he gained a scholarship at Clare College, Cambridge, and entered that University as an affiliated student.

His record as an undergraduate is exceptionally brilliant. In 1899 he was placed in the first class in Part I of the Natural Science Tripos, and also obtained First Class Honours in Chemistry and Second Class Honours in Physics in the B.Sc. examination of the University of London. In the following year he received a First Class in Chemistry in Part II of the Tripos, with the very rare distinction of a "star." In 1901 he was admitted to D.Sc. of London University. While still "in statu pupillari," he had obtained (in 1901) a University official appointment, that of Demonstrator to the Jacksonian Professor of Natural Philosophy, Sir James Dewar, which he held up to the time of his death. He was elected in due course (1902) to a Fellowship at Clare, of which college he subsequently became lecturer.

For eleven years Jones devoted most of his time and energy to teaching in the University laboratory, and to the direction and supervision of the science students of his college. His main task

in the chemical laboratory lay with undergraduates who were preparing for Part II of the Natural Science Tripos. It is in this work, perhaps, that he chiefly made his mark in the Chemistry School at Cambridge. It has been said of him that "for many years the advanced laboratory, where he was always at hand, practically revolved round him."

As a lecturer on organic chemistry Jones impressed his audience by the vast ground he was able to survey in the time at his disposal. His lectures, although not explanatory, were a model of concise expression. When, however, he was less constrained by shortness of time—in the lectures which he gave on his own special subject, stereochemistry—he got closely into touch with his audience, and could expound with a masterly lucidity. To the large elementary classes, as, for example, those he conducted for medical students, he was rather awe-inspiring; by a discipline which verged on the military, he made the class highly efficient.

But beyond this work with undergraduates Jones attracted a large and increasing number of graduates to carry on research under his direction. A long list of joint papers in various journals is evidence of his success with these students. He was not merely the teacher and director, but the guide and friend of the long succession of men who came under the influence of his vigorous and inspiring personality.

Jones was one of the most active and productive investigators of our day. In the last twelve years 1900-12, his name appears on no less than sixty separate publications. When the extent of his college and University duties was realised—he spent some five hours daily in the advanced laboratory, and was engaged for another two hours during term with the undergraduates of his college—it was not surprising to hear him say that a legal eight-hours' day would have made research impossible. Few, if any, were capable of such intense and continuous labour as he. In comparisons of the efforts of which men are capable, it was not uncommon to hear it said: "Jones is the hardest worker I have ever met."

Unlike many of his contemporaries, Jones had not visited foreign laboratories, or, in fact, other English Universities. He gained his experience of research entirely at Cambridge, working with Sir James Dewar and Dr. Fenton; with the latter he carried out his first experimental investigation on the "oxidation of organic acids in the presence of iron" (*T.*, 1900, **77**, 69). In a short time he struck out on a line of his own—the Stereochemistry of Nitrogen—and in 1904 he prepared a report on this subject for the British Association. This report, which is of a peculiar excellence, shows

at once Jones's great mastery of an intricate subject and his command of an exceptional lucidity of presentation. In 1907 and in 1909 he wrote the section on Stereochemistry for the annual reports of the Chemical Society. Whilst possessing the good qualities of his first publication, these later writings show in their selection and emphasis an increasing power of criticism. His familiarity with the important developments in chemistry other than his special subject, and his command of the methods of so-called 'physical chemistry' appear in these monographs as well as in accounts of his experimental investigations. Although his exposition was never anything but lucid—was, indeed, often graphic—his style was sometimes inelegant. It was, however, free from all affectation or mannerism.

The study of organic nitrogen bases led to the attempt to solve the difficult problem of the constitution and transformations of the alkol bases derived from the homologues of aniline, an inquiry which he had proposed to follow up.

Jones's exceptional powers are well shown by the fact that, while engaged on his own particular branch of chemistry, he was assisting Prof. Sir James Dewar in investigations of a very different kind, namely, of the metallic (nickel and iron) carbonyls. These researches had made Jones familiar with low temperature manipulations. This led ultimately to their discovery of carbon monosulphide. It was undoubtedly in this way that Jones's attention was directed to organic sulphur compounds, and as a result he began the investigation of the thio-oxalates, thiomalonates, and thiophosphates. His eminence as an investigator was recognised in his election to the Royal Society last year, at the early age of thirty-four.

Jones's activities were not confined to teaching and research. The wider problems of University administration and educational policy increasingly occupied his attention; to him the practical life of the outside world and its relation to education was always a subject of great interest. The increasing calls upon him in these spheres of labour prove that his capacity was realised. He played a particularly active part in the recent extension and reorganisation of the chemical laboratory at Cambridge. As a co-opted member of the Cambridge Appointments Board, he found scope for his peculiar facility in taking the measure of a man; his opinion on a candidate could never be neglected and had already become highly valued by the firms who employed men on his recommendation.

The movement for which he was largely responsible, to bring the policy of the London educational authorities into harmony with University ideals, owes much of its promise of success to his energy

and tact. Still further scope for his ability in affairs would have been found in the appointment, a few weeks before his death, to the Royal Commission to report on the use of oil fuel in the Royal Navy.

For several years Jones had few interests outside his work. He travelled a little, especially in Italy; he played golf, and was a member of the Cambridge and Royal Norfolk (Brancaster Links) Golf Clubs. He took great delight in gardening, and had a very good eye for the planting and laying out of grounds. A great and increasing interest was to arise when he discovered his peculiar power and inborn skill as a mountaineer—a discovery made almost accidentally in his native mountains as late as 1907. To this pursuit he brought all the thoroughness of his highly trained mind and the enthusiasm of his race. He set himself to learn the history of mountaineering, and to acquire the technique of the craft from the highest exponents, spending the greater part of his vacations in the Alps and in the mountains of North Wales. He soon developed a fine and accurate judgment of all the changing and varied conditions of the rocks, ice, and snow, and the weather of the Alps. Nothing seemed to escape his observation; he was the first to see the slight indications of changing weather or to recognise some rare bird or plant or some peculiarity in the rock formation. His knowledge of the Italian face of Mont Blanc was scarcely rivalled, and many new routes resulted from his thorough exploration of this region.

Nor was it only in intellectual power that his excellence was shown. Although his physique did not suggest muscular strength, he possessed a most remarkable endurance and the rare natural gift of a most delicate balance. His tirelessness and his speed are to be attributed, perhaps, not so much to inexhaustible vitality as to the economic use which his skill enabled him to make of his available force. His rapid, if not unique, rise to the very front rank of mountaineers was no surprise to those who had the opportunity of gauging the quality of the man.

He was elected a member of the Alpine Club in 1909, and was a member of the Committee of the Climbers' Club. The journals of both clubs, but especially of the Alpine Club, contain several papers in which his many daring explorations are recorded.

The very fact that he had passed over in so short a period the early stages in his initiation to mountaineering perhaps distinctly contributed to the accident in which he and his bride were killed. He did not take into account the possibility of a native Alpine guide slipping on an easy place. Whilst ascending the north ridge of the Mont Rouge de Peteret, near Courmayeur, on Thursday,

August 15th, 1912, their guide slipped and fell on Jones; the three dropped nearly 1000 feet to the Fresnay Glacier.

He married, on August 1st, 1912, Muriel Gwendolen Edwards, a member of the family to which the Bishop of St. Asaph and the late Dean of Bangor belong. She was a woman of great force and vitality, with rare gifts of taste and perception. A member of Newnham College, she had made chemistry her subject, and was the first woman to be elected a Fellow of the University of Wales. As enthusiastic as her husband in her love of the mountains, she appeared to their friends the perfect comrade for him in the intense life which opened before them.

The circumstances of Jones's life at Cambridge, and more especially his mountaineering, provided the opportunity for his characteristic genius for friendship. He was on terms of intimacy with a large number of men with whom his varied interests had brought him in contact, or who were attracted by his sympathetic temperament.

Remarkable as is the extent of his original work, it is yet difficult to decide whether Jones would have developed, as he gained more leisure and freedom, into a great original thinker and experimentalist. Perhaps because of his many abilities, his alertness, and his versatility, he tended to take up new and varied interests rather than to become entirely absorbed in his research. Jones was essentially a teacher; he took a minute personal interest in his students, and was never tired of discussing their characteristics and particular abilities, a quality which made him an excellent examiner. His ready sympathy and delicate tact made him easy of approach; few men were so often consulted or gave sounder advice.

That he was a man destined to exert a powerful influence in educational and scientific affairs, and to attain the highest eminence in University life there can be little doubt. The splendid tribute which is now being offered to his memory by a number of important firms, as well as by Cambridge colleagues and private friends, attest the esteem in which his character and intellect were held, and the value which was placed upon his training, as well as on his judgment, of men.

K. J. P. ORTON.



## JOHN WILLIAM MALLET.

BORN OCTOBER 10TH, 1832; DIED NOVEMBER 7TH, 1912.

THOSE who were so fortunate as to have seen Professor Mallet at the meeting of the Eighth International Congress of Applied Chemistry, at New York, were not prepared for the sad news of his death so soon afterwards, on November 7th, 1912; for in September he had seemed in good health. His illness was brief, and he died in Charlottesville, Virginia, where he had lived so many years. With his going, another of that older generation of chemists, who have done so much to make chemistry a power in the world, passes away; the world misses them keenly.

John William Mallet was born near Dublin, Ireland, on October 10th, 1832, the son of Robert and Cordelia Mallet. His father was a civil engineer, and Fellow of the Royal and other scientific Societies; and the son's interest in chemistry was early acquired from the reading of chemical classics in his father's library when a schoolboy. Before entering college he received private instruction in chemistry from Dr. James Apjohn, and at the age of seventeen he was admitted to Trinity, Dublin, where he obtained the degree of Bachelor of Arts in 1853, as gold medallist in Experimental Physics. The intervening years were profitably spent in a manner very different from that of the average collegian. His first paper on "A Chemical Examination of Killinite" was published in 1849, soon after his admission to college; and much time during the following years was spent in assisting his father in seismological investigations. During the summers of 1851 and 1852 he went to the University of Göttingen, where he studied chemistry under Wöhler, and received the degree of Ph.D. in 1855. He presented a thesis concerning the chemical composition of the Celtic antiquities in the Museum of the Royal Irish Academy.

After returning to and graduating at Trinity College, he went for the purpose of acquiring information for his father, to the United States; but he never became a naturalised American, remaining a British subject to the end. He was soon appointed professor of analytical chemistry at Amherst (1854), where a Göttingen friend, Dr. W. S. Clark, was in charge; but the following January Mallet accepted the position of chemist to the State Geological Survey at Tuscaloosa, Alabama. This change greatly influenced his life, for from that time forth his interest was allied with the South rather than with the North. In 1855 he became professor of chemistry in the University of Alabama, serving in that





capacity, with a brief leave of absence spent at Mobile, until the opening of the great Civil War. In the autumn of 1861 he enlisted as a private in a troop of Confederate Cavalry, but almost immediately was chosen as aide-de-camp on the staff of General Rodes. He was soon transferred to the artillery in May, 1862, and was in rapid succession captain, major, lieutenant-colonel, and later superintendent of the ordnance laboratories of the Southern States, from 1862 to 1865. His service to the Confederacy in supervising the manufacture of gunpowder was very great; he showed courage, wisdom, and patience in this task. In 1865, just before the close of the war, he was paroled as lieutenant colonel of the artillery.

After peace had been established he became professor of chemistry in the medical department of the University of Louisiana. The appointment was the outcome of a mission which he undertook, on behalf of some Northern financiers, to search for petroleum in this southern state. The result of the appointment was to direct his attention to medicine, in which he gained the degree of Doctor in 1868. In that year he was called to the University of Virginia, which became his final home, although not uninterruptedly. At first his work included analytical, industrial, and agricultural chemistry, but, as time progressed, his scope became broader and broader. He lectured at Johns Hopkins in 1877 and again in 1878, and during the winter of 1883-84 was professor of chemistry and physics, and chairman of the faculty in the University of Texas. The following year found him at the Jefferson Medical College in Philadelphia as professor of chemistry, but the unsatisfactory conditions there caused him to return in 1885 to the University of Virginia, which he never again left. In 1908 he was appointed professor emeritus at the age of seventy-six, but still kept his residence at Charlottesville, the beautiful seat of the university founded by Thomas Jefferson long ago.

Besides his services to the Southern States during the war, he undertook a number of other commissions of a public or semi-public nature, having served as judge in the bureau of awards at the Centennial Exposition in 1876 and been a member of the United States Federal Assay Commission in three years, 1886, 1888, and 1896. These last appointments showed that he and the Government had generously outlived the jealousies of the war. He belonged to many chemical and other learned societies besides the Chemical Society, being an honorary member of a number of them. He was a fellow of the Royal Society, of the College of Physicians of Philadelphia, of the Medical Society of Virginia; associate fellow of the American Academy of Arts and Sciences, and fellow of the American Association for the Advancement of Science, member of

the Society of Arts in London, American Chemical Society (of which he was President in 1882), Chemical Society of France, German Chemical Society, American Philosophical Society of Philadelphia, and several other local societies, including several in Mexico and Brazil. He received the honorary degree of L.L.D. from five institutions of learning, namely, William and Mary College, University of Mississippi, Princeton, Johns Hopkins, and the University of Pennsylvania.

His interest in the South was emphasised and strengthened by his marriage to Mary E. Ormond, the daughter of an Alabama judge, in 1857, and again, after the death of his first wife in 1886, to Mrs. Joséphine (Pagès) Burthe, of Louisiana, in 1888, who with two of the three children by his first wife survives him. His first-born son, John Ormond Mallet, died at an early age.

The scientific work of Professor Mallet covered a wide field. Besides his studies in general and applied chemistry and in chemical mineralogy, which were incidents in his work for the Southern States and in various technical professorships which he held, he spent much time on various other analytical problems of interest; for example, he devised methods for the determination of organic matter in potable water. He added to our knowledge of meteorites, and of many rare terrestrial minerals, by careful analysis. He studied the occurrence of silver in volcanic ash from South American volcanoes. Theoretical problems also interested him greatly; for example, he determined the density of solid mercury and the molecular weight of hydrochloric acid. He probably will be remembered chiefly in the field of pure chemistry through his work on the atomic weights of lithium, aluminium, and gold. The work on aluminium was particularly comprehensive and thorough, and has remained our chief basis for a knowledge of this atomic weight ever since its publication in 1880. The work on lithium, one of the first investigations in a field which has since been very much cultivated in America, was carried out in 1856. It is interesting to note that this work, although somewhat crude, was far better than that of Stas, as indicated by the most recent investigation of this subject. His value 6.943 is very near the value which at present seems most probable, namely, 6.939, whereas Stas found the widely divergent number 7.01, making mistakes in this case perhaps more serious than in any other. Mallet's interest in atomic weights appeared also in the admirable lecture delivered in memory of J. S. Stas in 1892 by request of the Chemical Society. Besides all this purely scientific accomplishment, he carried out a large amount of technical and expert work. He served as expert witness in many medico-legal cases involving various forms of poisoning, as well as

took part in numerous commercial cases involving the value of iron ore, the pollution of river water, and many other chemical questions. As analytical and consulting chemist also, he performed many analyses and gave advice concerning a great variety of chemical processes, doubtless adding much to the efficiency of his client's undertakings.

This brief record does but scanty justice to a life full of manifold usefulness and high endeavour. A more complete biography and a complete bibliography of Dr. Mallet's publications is to be found in the January (1913) issue of the sixth volume of the Alumni Bulletin of the University of Virginia. Out of this paper the following extract from a vote of the Faculty of the University is reprinted:

"He stood like a rock for principle, high character, truth, and integrity. His influence has been for courage, strength, and steadfastness of purpose to meet the problems of life earnestly and hopefully. Great as have been his world-wide acknowledged intellectual achievements in science, these seem to fade into insignificance when compared with the impress of character which he has stamped upon the generation of men who have sat at his feet in this University. He was the soul of honour, truth, and courage; he hated sham, deceit, and charlatanism in all their forms, and, regardless of the consequences, never permitted himself to swerve a hairbreadth from what he recognised to be a principle. He lived his life before all men as a manly man and a kindly gentleman without fear and above reproach."

THEODORE W. RICHARDS.

### HENRY DE MOSENTHAL.

BORN 1850; DIED DECEMBER 17TH, 1912.

HENRY DE MOSENTHAL was born at Port Elisabeth, South Africa, in 1850, and died on December 17th last. During the greater part of his life he was connected with the explosives industry, having been technical secretary to the Nobel Dynamite Trust Company, Ltd, since its formation. For many years previously he had associated with Alfred Nobel, the inventor of dynamite, and many of his researches had reference to the explosives industry. De Moseuthal was an expert microscopist, as well as an experienced technical chemist, and his investigations have contributed much to the progress of the industry with which he was associated. Most of his papers were read before the Society of Chemical Industry, and were published in the *Journal* of that Society. Among the

more important of these may be mentioned "Observations on Cotton and Nitrated Cotton," published in 1904, 1907, and 1911. A visit to South Africa furnished the material for an interesting paper on the "Treatment of Gold Ores at the Witwatersrand (Transvaal) Gold Fields," published in the *Journal of the Society of Chemical Industry*, 1894. Besides his published researches, De Mosenthal undertook many other investigations in industrial chemistry, which were not published. One of these was a careful inquiry into the occurrence of deposits of saltpetre in South Africa, and he also made an exhaustive inquiry into the methods by which a less inflammable substitute for celluloid could be produced. De Mosenthal's researches were extended beyond the limits of pure and applied chemistry, one of his earliest papers being on the structure of the eye, a contribution to science which was enriched by numerous excellent microphotographs. A shrewd observer and a good linguist who had travelled much, De Mosenthal was an excellent conversationalist. He was a bachelor and a member of the Savage Club.

W. F. REID.

#### BENJAMIN EDWARD REINA NEWLANDS.

BORN JANUARY 23RD, 1842; DIED AUGUST 7TH, 1912.

BENJAMIN EDWARD REINA NEWLANDS, youngest son of the Rev. William Newlands, was born at Southwark on January 23rd, 1842. His mother was of Italian descent. Both he and his brother John (who will be remembered in connexion with the discovery of the periodic law of the elements) studied under Professor A. W. Hofmann at the College of Chemistry, and at an early age they started in practice as analytical chemists in London. Benjamin became an assistant to Professor Heaton at Charing Cross Hospital in 1862 and to Professor Way, of the Royal Agricultural Society, in 1863. His bent was always, however, towards technology, and at the end of 1863 he was appointed chemist to Messrs. J. Gibbs and Co., manure makers, Victoria Docks. He held the appointment of manager at this works from 1869 to 1873, after which year he became manager at Messrs. J. Duncan's sugar refinery, Clyde Wharf, Victoria Docks, his brother John being chief chemist. This position he retained until the close of the refinery (then the largest in the United Kingdom) in 1887, when the brothers once more embarked upon a professional career as analytical and consulting chemists. Well known as they were in the sugar industry, the brothers Newlands soon built up a good practice, chiefly concerned with sugar technology, not only of this country but also of the

Colonies and India. After the death of John Newlands, the writer was in partnership with Benjamin for five years. Benjamin Newlands was a very active member of the Society of Chemical Industry, having served on its Council and most of its committees from its inception. He will be remembered by his professional brethren for his wide practical knowledge no less than for his sound common sense, which was tempered by a characteristic and rare geniality of manner.

ARTHUR R. LANG.

### JOHN PATTINSON.

BORN FEBRUARY 13TH, 1828; DIED MARCH 28TH, 1912.

JOHN PATTINSON was born at Alston, in Cumberland, on February 13th, 1828. He spent his schooldays at the Grammar School there, and whilst he was quite a youth his distant kinsman, Hugh Leo Pattinson, well known as the inventor of the Pattinson process for desilverising lead, invited him to come to Newcastle, and placed him in the laboratory of the Felling Chemical Works on the Tyne, where the manufacture of alkali by the old Leblanc process was carried on, with its attendant manufactures of sulphuric acid, hydrochloric acid, and bleaching powder. After ten years' association with the alkali manufacture, John Pattinson went to Middlesbrough under Isaac Lowthian Bell; and he there acquired an intimate knowledge of the iron and steel manufacture as it was practised in these early days—the days when Bell was beginning that long series of researches which were collected later in his classic "Chemical Phenomena of Iron Smelting." In 1858, Pattinson left Middlesbrough and returned to Newcastle, where he took over the practice of analytical and consulting chemist then carried on by William Crowder, in the Side, and in that work, with two successive removals to larger premises, he continued until his death. In 1890 he was joined in partnership by his eldest son, Dr. H. S. Pattinson (died 1901), and in 1901 by the present writer. In 1868 he was instrumental, along with his brother-in-law, Mr. J. W. (now Sir Joseph) Swan, the late Barnard Proctor, and others, in founding the Newcastle Chemical Society, which had a useful and honourable career until, in 1882, it merged its separate existence in the Society of Chemical Industry; he was treasurer of that Society during the whole fourteen years of its existence, was its president during 1874-75, and published papers in its Transactions on the determination of peroxide of manganese, on the quality of the small coal used on the Tyne, on the determination of arsenic in copper, and other subjects. At the meeting of the British Associa-



tion in Newcastle in 1863, he read a paper on the pyrites used on the Tyne; he was also a member of a Committee of that Association on the question of the illuminating power of coal gas. His firm having a large practice in the assay of iron and manganese ores, he was led to investigate the conditions under which manganese can be precipitated as peroxide, and described before this Society in 1879 a method for manganese determination, which is still in daily use in laboratories where these determinations are made, and is of great accuracy and trustworthiness. Several other papers and notes by him alone, or with H. L. Pattinson or J. T. Dunn, are found in the *Society of Chemical Industry's Journal*. He was among the earliest to hold municipal appointments connected with chemistry; he was made Gas and Water Examiner for Newcastle in 1863, and Food Analyst in 1871; later, when the Food and Drugs Act of 1875 was passed, he was appointed Public Analyst for Newcastle, for the County of Northumberland, and for other boroughs near. He was a Fellow of this Society since 1863, and had been a Vice-President, and a Vice-President of the Society of Public Analysts; was an original Fellow of the Institute, for which he had served on the Council and as Censor; was an original member of the Iron and Steel Institute; and was a Vice-President of the Literary and Philosophical Society of Newcastle.

He was a man of very varied activities outside his profession—a Justice of the Peace, and an administrator in various philanthropic and charitable institutions; an enthusiastic musician, and president of the local Choral Union; and had the high esteem of all who came into contact with him, no less for his kindness of disposition than for his incorruptible uprightness and straightforwardness.

J. T. DENX.

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#### ARTHUR RICHARDSON.

BORN 1858; DIED JUNE 1ST, 1912.

DR. ARTHUR RICHARDSON was born in 1858, and belonged to a well-known Quaker family. He was elected a Fellow of the Chemical Society in 1885. He first studied chemistry under Prof. Crum Brown in the University of Edinburgh, but when in 1876 Dr. E. A. Letts was elected to the Professorship of Chemistry at the University of Bristol, he entered as a chemical student under Prof. Letts. In 1883 he spent a year under Prof. Wislicenus in Würzburg. In 1886 he obtained the Ph.D. degree at Freiburg University, and he then returned to University College, Bristol, as an assistant, remaining there until 1896. In 1888 he was made

an Associate of University College, Bristol. Leaving Bristol in 1896, he went to India, associating himself with the cult of Esoteric Buddhism, and gave up the remainder of his life to work connected with teaching at the Central Hindu College, Benares. There he taught chemistry, and for many years was head of the College.

During the last ten years of his life, owing to growing ill-health and lack of opportunity, he did little research, but he was always keenly interested in what was going on in the chemical world.

It was before he left England that the most important of his investigations were carried out. These mostly centred round one idea—the action of light on various substances; and on this subject he published a good many papers. His best piece of work was on the measurement of light intensity by the expansion of chlorine when exposed to sunlight, and he constructed an automatic registering apparatus that would record continuously the actinic intensity of the light under all conditions of weather throughout the year. Several other papers were of considerable interest: the action of light on the hydrazides in presence of oxygen, the decomposition of silver chloride under the influence of light, and the action of heat on nitrogen peroxide, were all excellent work. Dr. Richardson was a true investigator, but he was always far more interested in the mechanism of reactions than in the manufacture of new substances; nevertheless he was an expert worker, and many of his pieces of apparatus were marvels of ingenuity.

J. N. COLLIE.

#### JOHN WADE.

BORN JANUARY 13TH, 1861; DIED AUGUST 15TH, 1912.

JOHN WADE was born at Deptford on January 13th, 1861. A tragic accident which he suffered on the 28th of July last year brought to its end a life still in its prime and full of the promise of further achievement. Wade was riding a motor-cycle at Otford when he collided with a cart which had suddenly turned a corner of the road. A shaft struck him violently in the upper part of the chest, fracturing four ribs and damaging a lung. After surviving for three weeks and giving his friends good reason to hope for his ultimate recovery, he died suddenly on August 15th, 1912, as the result of a pulmonary embolism.

To appraise with full justice Wade's accomplishment as a scientific worker and teacher, it is necessary to realise that he was intellectually self-made. In his scientific development he owed to others as little as it is possible for any man to owe. Wade's father was a highly intellectual man, of pronounced artistic tastes, and no small power

of artistic accomplishment. He had a circle of cultured friends, and John Wade had the advantage, when a youth, of living in a cultured household. But his father, who depended upon his salary as an official of the Kent Water Works Company, was unable to afford him any but an inexpensive education, which had to stop when his schooldays, spent at Aske's School, Hatcham, came to an end.

He entered, when a youngster of less than sixteen, the private laboratory of Sir Thomas (then Dr.) Stevenson, at Guy's Hospital, prepared to make himself generally useful. He found there Mr Richard Bodmer, the present Public Analyst for Bermondsey and Northampton, who was then, and for many years afterwards, Dr. Stevenson's private assistant. Wade's career was not then chosen, and he went to the laboratory without definite aims, and merely to await developments. The first development came when the then lecture assistant at Guy's lost his reason and offered personal violence to the lecturers. Wade temporarily filled the gap thus rendered inevitable, and after a very short interval of, at most, a few months, spent in the laboratories of the Royal College of Science, he was definitely appointed to the office, and remained in it for about six years.

The only educational scientific lectures he ever attended—save a few connected with evening classes at the Birkbeck Institute—were those he thus heard as an untaught lecture assistant, and so far as he listened to them at all it was as a youth not yet aware that chemistry was to remain his life's pursuit. He was privileged, it is true, to assist such able teachers as Debus, Thomas Stevenson, Charles Edward Groves, and Reinold, and doubtless such contact as he had with them carried inspiration; but all were busy men of whom Wade saw little in the laboratory, and with whom his relations were of a quite formal sort. He never, at any time of his life, even saw a foreign laboratory, and never once shared the responsibility of research with a senior; never, indeed, saw any research in progress save that inspired by himself.

For a year or two after his appointment as lecture assistant he made no attempt to acquire any real knowledge of chemistry, being but a prankish boy, although a very clever one. He was somewhat plagued at this time by a mountain of flesh, weighing twelve stone when only sixteen. Although he completely got rid of this trouble later on, it was only kept under by careful habits in diet. By 1883 his intellectual development had greatly progressed, and he began to take serious thought for the future. He gave his evenings to successful study for London Matriculation, and afterwards attended classes at the Birkbeck Institute while preparing for the Intermediate Science Examination. In 1886 he gave up the position of lecture assistant, and, for the moment, gave up also all idea of a

scientific career. He thought of entering the Patent Office, and worked for a while in preparation for the necessary examinations. A little later he had some notion of a non-collegiate course at Cambridge, and resided in the town for a few weeks during Long Vacation; but he experienced some discouragement, and gave up the enterprise. At this period his mind was much unsettled; he felt he was marking time, and was, not unnaturally, depressed. He spent a little time in the laboratory of F. J. Lloyd, and for about a year was chemist in a paper works at Northfleet. In 1890, having been a little earlier appointed Gas Examiner under the London County Council, he entered into partnership with his earliest colleague, Richard Bodmer, and shared for a year his laboratory in Southwark Street. About this time Wade took the B.Sc. degree.

Meanwhile his merits had not been overlooked or forgotten at Guy's, and when, in 1893, Groves ceased to participate in the practical teaching, and the appointment of an Official Demonstrator became necessary, the authorities of the medical school sought Wade's services. He accepted the post with delight, and now, for the first time, felt that ease of mind which comes with security and a defined aim. Retaining his Gas Examinership, he felt able to marry, and took to wife Clara Threadgold. He lived first at Purley, but later, in order to be near his work, he settled in Trinity Square, S.E., and remained there until, in recent years, he went to live at Downe.

It should be understood that, not until the time of his appointment as Demonstrator at Guy's, when he was already twenty-seven years old, did Wade's mind come seriously to grips with the subject he was to know so well and teach so admirably.

He set to work to organise the practical teaching of the medical school laboratories on original and stimulating lines, and, when he felt that this task had been accomplished, he began to gather material for his text-book. During the slow writing of this book, which he accomplished with infinite pains and labour, Wade made himself a profoundly learned organic chemist. He went to original sources for every fact, and being gifted with a most retentive memory, and an active imagination, he stored an immense amount of knowledge, and at the same time was greatly stimulated by prolonged contact with the original writings of master chemists. His marked critical power and sense of proportion marshalled the facts of the science into an ordered edifice within his mind, and he became, as I have claimed, really learned in his subject. He produced an admirable book, but, what is more important, the writing of the book made its author an enthusiast. The first edition of the book appeared in 1897, the second in 1905, and the third in 1911. It has been translated into other languages, including Portuguese. Wade

became joint lecturer on chemistry in 1898, and in 1901, on the retirement of Mr. Groves, he became sole lecturer and head of the Department.

Wade had skilful hands and an instinct for accuracy in all kinds of experimental work. In his earlier days as a responsible teacher, he spent an immense amount of time in rehearsing and testing methods, and much labour spent in improving them never had the reward of publication. He was amply stocked with ideas, and began research immediately after he had commenced to write his book; but, as I shall later point out, his preoccupations and his temperament made original work for some years very difficult.

He was early interested in the question of the constitution of hydrocyanic acid, and, like many others, possessed at one time the hope of being able to prepare its unknown isomeride. As the first fruits of work done in this connexion, he published, with L. C. Pauting, in 1898, a brief paper, in which it was shown that in the action of sulphuric acid on potassium cyanide, a practically quantitative yield of either hydrocyanic acid or carbon monoxide respectively can be obtained by suitably varying the concentration of the acid (T., 1898, **73**, 255). In 1900 appeared a note on the constitution of hydrocyanic acid, which was eventually expanded into the highly important paper (T., 1902, **81**, 1596), "On the Constitution of Metallic Cyanides as deduced from their Synthetic Interactions." Dealing with the familiar circumstance that while the alkali cyanides when reacting with alkyl sulphates or iodides yield nitriles, the cyanides of the heavy metals yield in similar circumstances alkyl isocyanides, Wade showed that it is logically impossible to explain the facts by assuming the occurrence of isomeric change or by means of Laar's hypothesis of tautomerism in the molecule of hydrocyanic acid. Having shown that all the evidence goes nevertheless to prove that the alkali cyanides, no less than silver cyanide, have themselves the carbylamine structure (although hydrocyanic acid is a nitrile), he explained all the phenomena involved by an ingenious extension of Nef's hypothesis concerning the intermediate formation of additive compounds. The paper contains an account of abundant original experimental work, some of which illustrates the author's genius for defining the exact experimental conditions necessary to produce a desired result.

Wade's subsequent work dealt for the most part with physical chemistry, and was mainly concerned with the properties of mixtures with a constant boiling-point. Various circumstances directed his efforts into this channel. The subject appealed first of all to an intellectual prepossession which finds reference below. Then, in his cyanide work, he came upon a case which impressed him with the practical importance of these mixtures. He at one time

thought he had successfully separated nitriles from *isocyanides* by fractional distillation, but later found that the supposed *isocyanide* fractions were really lyotropic mixtures of nitriles, alcohols, and hydrocyanic acid, containing but little of the *isocyanides* (compare p., 1900, 16, 156; T., 1902, 81, 1598). Again, in 1904, he had undertaken, in conjunction with H. Finnemore, to find an explanation for the fact that chloroform made from acetone had properties as a practical anæsthetic mysteriously inferior to those of the product from alcohol. The practical end of the research was attained when it was found that the latter always contained traces of ethyl chloride which improved its anæsthetic action, and when it was shown that the addition of the same substance to "acetone chloroform" brought it into line with the alcohol product. In the course of the very interesting work involved in this investigation (T., 1904, 85, 938) Wade isolated several ternary and binary mixtures, gaining great skill in fractional distillation and an increased interest in the subject. In the following year he published a paper on the influence of water and alcohol on the boiling point of esters (T., 1905, 87, 1656). In this is first described a method for the preparation of esters by a continuous process, and next a very careful quantitative study of the fractional distillation of ethyl acetate in the presence of alcohol and water, during which ternary and binary mixtures of constant boiling point were isolated, and their properties studied.

In 1909 Wade and Finnemore turned their attention to ethyl ether, having observed that while the boiling points found for this substance by modern observers were concordant, the variations in the statements as to its density lay outside the limits of experimental error. The outcome of the work (T., 1909, 95, 1842) was a proof that ether forms a binary mixture with water, which boils, with characteristic constancy, 0.35° lower than pure ether. Unless therefore all but traces of water is first removed, it is impossible to prepare the pure substance by fractional distillation. Ternary lyotropic mixtures of alcohol, water, and ether were shown not to exist, but the presence of alcohol was found to raise the boiling point of the above binary mixture as well as of ether itself.

During these various studies of fractional distillation, Wade wished to determine the specific gravity of individual fractions with the highest possible accuracy, but found it difficult, in spite of great experimental care, to obtain results concordant within the required limits. He traced the errors to an inadequacy in the formula ordinarily used for correcting for the buoyancy of air, and in a paper published with R. W. Merriman, who had become his Demonstrator, he describes some careful experimental work done in connexion with this matter, and proposed a new correction formula which yields satisfactory values (T., 1909, 95, 2174). By this time, having

realised by experience the difficulties which occur in the endeavour to isolate constant mixtures of minimum boiling point, and wishing in particular to study the effect of variations in pressure on the physico-chemical "individuals" which were interesting him, Wade felt the need of special apparatus. His needs led him to construct the "manostat," as he called it, an instrument capable of continuously maintaining in the distillation apparatus pressures high or low with a maximum deviation of  $\pm 0.2$  mm. from the mean. In the paper which describes this (Wade and Merriman, T., 1911, 99, 984), other very ingenious adaptations of apparatus to the requirements of the problem will be found. Wade and Merriman (*ibid.*, 997) now submitted mixtures of alcohol and water to distillation under various pressures. They found that the composition of the constant boiling-point mixtures ("azeotropic," or temporarily hydropotropic mixtures, as it was now proposed to call them) varied continuously with pressure, and they got no indications, at any time, of the transition of such a mixture into a more permanently hydropotropic substance ("chemical individual") on the lines of suggestions by Wald and Ostwald (Ostwald, T., 1904, 85, 511). They found that in the case of mixtures of minimal boiling point the percentage of water present increased with the pressure, whilst they got evidence that at pressures below 100 mm. no azeotropic mixtures of alcohol and water are formed at all, so that it should be possible to obtain anhydrous alcohol by fractional distillation at such low pressures. In a large scale rectifying apparatus, they point out, it is possible to reduce the percentage of water to a fraction of 1 per cent. by one or two rectifications under 50 mm. pressure.

The remaining papers were published after Wade's death by his colleague, Mr. Merriman (T., 1912, 101, 2429, 2438). They contain an account of the purification, density, expansion, and vapour-pressures of ethyl acetate, the work described showing the meticulous care and experimental resourcefulness of all that had preceded it.

Everyone will admit that the quality of Wade's scientific work was of a high order and worthy of his undoubted genius; but it may be felt that its actual amount was not proportionate to his characteristic industry. If this be true, it is because his output was limited by his temperament and by the large amount of extraneous work in which he engaged. He inherited his father's artistic temperament, and it made him crave for a finality and perfection in his work which in a scientific investigation is so rarely possible. He always hesitated to publish, even when his note-books were full.

On the other hand, for some years he spent a great deal of time on very admirable work done for the Local Government Board in connexion with the subject of ship disinfection (*Brit. Local Govt.*

*Bd. Rep.*, 1907), and, as is well known, he devoted himself continuously to the politics of the London University. In his opposition to the concentration of Preliminary Science teaching, he was moved by the belief that it was against the interests of the medical schools as institutions, no less than those of the teacher and the taught; and he was able to convert the majority to his opinion. The strong support he gave to the maintenance of the External Side of the University arose partly from sentiment—for he was strongly indebted to that side—but it was based also upon thought and conviction. He was able to give impressive evidence in its favour before the Haldane Commission. He gave his time to those controversies from a sense of duty, but it must be admitted that he took a pleasure in fighting for his beliefs; for, combined with his artistic inheritance, he carried a temperamental legacy of a quite different kind. His paternal grandfather was, in his time, a keen politician, and a noted protagonist in the struggle for civil and religious liberty in South London. There is no doubt that John Wade enjoyed being in the arena almost as much as he enjoyed giving attention to the fifth decimal place in his laboratory work. In fact, the combination in him of the artist, scientist, and man of affairs was somewhat remarkable; the various sides of him were not always known to the same people.

As a scientific thinker Wade was especially characterised by an earnest belief that chemistry ought to be liberated from the shackles of atomistic hypotheses. He held that all the stoicheiometric laws and all that is special in chemical phenomena are capable of explanation from a dynamical point of view. I must point out that he held these views when quite young, long before Ostwald had delivered his Faraday lecture in 1904, and before the writings of Franz Wald (that "solitary philosopher," as Ostwald calls him) were known to him. I remember hearing Wade expound his views in 1895, and I realised then, as often later on, how great was his tendency to be preoccupied with the widest and most general aspects of his science.\* He always intended that his own researches should bear upon the above great matter; hence his great interest in lyotropic mixtures, which, had he been spared, were to have received much more attention at his hands. The sorrow felt by his friends for his tragic death was intensified by their knowledge of the fact that, freed from his preoccupations, and recently provided with an admirably efficient laboratory, he was beginning what might well have proved the most prolific period of his life as an investigator. His mind remained alert and elastic, and his energy and enthusiasm were unabated.

\* I venture to quote the above paragraph from an article written by myself in the *Gen. Hospital Gazette* for August 31, 1912.



Wade became a Fellow of the Chemical Society in 1890. He was a member of the Council from 1905 to 1909, and served upon the Publication Committee. He was admitted Fellow of the Institute of Chemistry in 1891, and received the Doctorate of the London University in 1902. He leaves a widow and one son—a youth of great promise.

F. GOWLAND HOPKINS.

#### WILLIAM ORD WOOLTON.

BORN OCTOBER 5TH, 1884; DIED OCTOBER 17TH, 1912.

By the premature death of this promising young chemist our science has lost one of its most enthusiastic workers. A son of the late Staff Engineer W. W. Woolton, R.N., he was born at Portsmouth on October 5th, 1884. He was educated at Sir Joseph Williamson's Mathematical School, Rochester, where he became Head of the School. Having gained the Governors' Leaving Exhibition, he spent a short time at the Birkbeck College, and in 1902 he entered the Royal College of Science at South Kensington. Having passed with distinction through the curriculum, he was appointed, three years later, one of the "teaching scholars," and in that capacity assisted in giving practical instruction in the laboratory of the college. About the same time he took the degree of B.Sc.Lond., with honours in chemistry. In 1906 he was promoted to the position of one of the assistant demonstrators at the time of the removal of the chemical department to the new buildings. In 1910 he was chosen to fill the vacant post of Demonstrator at St. Bartholomew's Hospital Medical School, and there he remained until seized with fatal illness. He died on October 17th, 1912.

Mr. Woolton was a born investigator. His interest in science began to show itself early in his school career, and after he became a student at the Royal College of Science he soon attracted the notice of his teachers by his intelligent and ardent devotion to experimental work.

His first independent investigation was embodied in a paper on "Aromatic Amides and Imides," which appears in the Transactions of the Chemical Society for 1907. Other papers followed in 1910 and 1911, also in the Transactions. Possessed of an ever active mind, he was never so happy as when engaged on new problems, and this enthusiasm he was often able to communicate to the students under his charge, and by whom he was much esteemed and respected.

His family wish it to be known that he was to the last a devout member of the Church of England. His last distressing illness, which he knew to be hopeless, he bore without complaint and with quiet fortitude.

W. A. T.

*Ed. Rep.*, 1907), and, as is well known, he devoted himself continuously to the politics of the London University. In his opposition to the concentration of Preliminary Science teaching, he was moved by the belief that it was against the interests of the medical schools as institutions, no less than those of the teacher and the taught; and he was able to convert the majority to his opinion. The strong support he gave to the maintenance of the External Side of the University arose partly from sentiment—for he was strongly indebted to that side—but it was based also upon thought and conviction. He was able to give impressive evidence in its favour before the Haldane Commission. He gave his time to those controversies from a sense of duty, but it must be admitted that he took a pleasure in fighting for his beliefs; for, combined with his artistic inheritance, he carried a temperamental legacy of a quite different kind. His paternal grandfather was, in his time, a keen politician, and a noted protagonist in the struggle for civil and religious liberty in South London. There is no doubt that John Wade enjoyed being in the arena almost as much as he enjoyed giving attention to the fifth decimal place in his laboratory work. In fact, the combination in him of the artist, scientist, and man of affairs was somewhat remarkable; the various sides of him were not always known to the same people.

As a scientific thinker Wade was especially characterised by an earnest belief that chemistry ought to be liberated from the shackles of atomistic hypotheses. He held that all the stoicheiometric laws and all that is special in chemical phenomena are capable of explanation from a dynamical point of view. I must point out that he held these views when quite young, long before Ostwald had delivered his Faraday lecture in 1904, and before the writings of Franz Wald (that "solitary philosopher," as Ostwald calls him) were known to him. I remember hearing Wade expound his views in 1895, and I realised then, as often later on, how great was his tendency to be preoccupied with the widest and most general aspects of his science.\* He always intended that his own researches should bear upon the above great matter; hence his great interest in lyotropic mixtures, which, had he been spared, were to have received much more attention at his hands. The sorrow felt by his friends for his tragic death was intensified by their knowledge of the fact that, freed from his preoccupations, and recently provided with an admirably efficient laboratory, he was beginning what might well have proved the most prolific period of his life as an investigator. His mind remained alert and elastic, and his energy and enthusiasm were unabated.

\* I venture to quote the above paragraph from an article written by myself in the *Gen. Hospital Gazette* for August 31, 1912.

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W. A. T.

LXXVIII.—*The Action of Tartaric Acid on Tin in the Presence of Oxygen.*

By ALFRED CHASTON CHAPMAN.

IN connexion with a technical investigation with which I was concerned four years ago, I had occasion to ascertain the effect of aqueous solutions of tartaric acid on tin under varying conditions. In the course of the work I noticed certain phenomena which I could not understand, and which appeared to me to be of sufficient interest to justify a more detailed and systematic study of the reactions involved. To this end I decided partly to immerse rods of pure tin in moderately dilute aqueous solutions of the acid, and as the action was to take place at the ordinary temperature and would be a very slow one, I thought that the most convenient method of conducting the experiments would be to employ deep wide-mouth bottles closed with corks, the tin rods being passed through holes bored in the corks, and so held in a vertical position in the acid solution. The bottles had a capacity of about 150 c.c., and in each there was one rod. It should be stated that in all cases the corks were bored entirely through, and a very short length of each rod projected as a rule above the top of the cork. Twenty of the bottles contained a 5 per cent. solution of the pure acid in distilled water, whilst in five a 10 per cent. solution was employed. The tin was the purest supplied by Kahlbaum, and on analysis was found to contain only minute traces of impurities. The rods were approximately 7 mm. in diameter, and the length actually immersed in the liquid was usually about 10 cm. The bottles contained the acid solution to the level of their shoulders, so that when the cork with its rod of tin was inserted, each bottle contained a few c.c. of air between the level of the liquid and the bottom of the cork. I have felt it necessary to enter into these details, since they have an important bearing on the results obtained. The bottles were all exposed to full daylight and kept at ordinary atmospheric temperatures. At the end of some months the surfaces of the rods were seen to be distinctly etched, and later small, colourless crystals formed on some of the rods. Similar crystals also occurred at the bottom of some of the bottles, and at the time I thought that these had become detached from the rods. Later I found that, although this did account for some, there could be no doubt that a proportion of the crystals had never formed on the surface of the metal. The action was evidently a very slow one, and the bottles were left unopened for about three years. At the

end of that time it was found that in the bottles containing the 10 per cent. solution of the acid very little action had occurred, and in no case had the crystals formed as readily as in the weaker solutions.

In the light of what was subsequently learned as to the nature of this action, it will be seen that this may have been to some extent a matter of accident. The bottles containing the weaker acid could be divided into three groups: (1) Those in which no apparent action had taken place, the tin rods being perfectly bright, though sometimes slightly etched, and the contents of the bottles entirely free from crystals. (2) Those in which the tin had obviously been very much acted on, the rods being more or less covered with well-formed crystals, whilst in some a further amount of crystalline deposit occurred at the bottom of the bottles. In these cases the acid solution was colourless, and had very little odour. (3) In these the tin had been very considerably acted on, the rods being closely coated with crystals, which were, as a rule, smaller and less well defined than those in the preceding group. In four of the bottles the rods had been completely eaten through at the surface of the liquid, and the acid solution was distinctly coloured, the colour ranging from a pale straw colour to a deep orange-red with a slight greenish fluorescence. These solutions had a distinct odour suggestive of slightly charred sugar. At first I thought that the different behaviour of the metal in these various experiments might be due to slight differences in purity, but very careful analysis showed no appreciable difference between the degree of purity of the rods which had been acted on and those which had not, and an attempt to increase the action by wrapping portions of the rods with platinum foil gave entirely negative results. Some of the crystals, when dried to a constant weight in a vacuum desiccator over sulphuric acid, gave the following results on analysis:

0.2135 gave 0.121  $\text{SnO}_2$ . Sn = 44.66.

0.2296 „ 0.1303  $\text{CO}_2$  and 0.036  $\text{H}_2\text{O}$ . C = 17.85; H = 1.74.

$\text{C}_4\text{H}_4\text{O}_6\text{Sn}$  requires Sn = 44.57; C = 17.98; H = 1.50 per cent.

A further portion of the crystalline substance, when dissolved in dilute hydrochloric acid, produced exactly the same rotation of the plane of polarised light as a solution containing the equivalent quantities of tin and tartaric acid in the proportions necessary to form stannous tartrate. The crystals consisted therefore, as might have been expected, of stannous tartrate, a substance which, so far as I am aware, has never previously been obtained in this manner. Inasmuch as the corrosion of the rods was most marked at the surface of the liquid, it appeared very probable that oxygen was concerned in the process, and an experiment was devised to test

this point. A roll of pure tin foil was partly immersed in a 5 per cent. aqueous solution of tartaric acid contained in a small glass tube, which was sealed on to a manometer, so that any absorption of the oxygen could be measured. Within a very short time of commencing the experiment the pressure began to fall, and at the end of one day it had become reduced from 929 mm. to 845 mm., and at the end of two days it had fallen to 827 mm. (a point which corresponded with the absorption of more than half the oxygen). The tin was greatly corroded at the surface of the liquid, whilst the immersed portion remained perfectly bright, and was apparently unattacked. At the same time a quantity of a white, flocculent substance separated. This entirely confirms the statements of Hall (*J. Amer. Chem. Soc.*, 1883, **4**, 440) and of Lehmann (*Arch. Hygiene*, 1907, **63**, 67), that in the absence of oxygen, tartaric acid has very little action on metallic tin. An examination of the liquids in which the tin rods had been immersed was next made. It was found that, on adding a solution of calcium chloride to the brown liquid, a buff-coloured, gelatinous precipitate was obtained, whilst no precipitate was formed in the colourless solutions. As it was thought that this might be the calcium salt of some organic acid formed by the action of the tin, a quantity was prepared, filtered, thoroughly washed with water, and dried at 100°. It was noticed that during the washing, as soon as almost the whole of the excess of calcium had been removed, the precipitate commenced to pass through the paper, giving an opalescent filtrate. The dry substance, which had a yellow colour, was found to contain 62 per cent. of tin, and to be practically free from carbon.

It was then observed that sodium chloride, sodium acetate, hydrogen chloride, and other electrolytes all produced a similar precipitate, and it became evident that the liquid consisted of a colloidal solution of some oxide of tin. A quantity of the brown solution was therefore put into a parchment thimble, which was surrounded by distilled water, the water being changed daily until the dialysate was no longer acid. This dialysate was found to contain tartaric acid, but no trace of tin. It was colourless, and remained colourless even when concentrated to a very small volume. The liquid in the thimble when evaporated to dryness left a yellowish-red, transparent mass, which was free from organic matter, and when dried at 100° contained 64.5 per cent. of tin. It was very hygroscopic, rapidly absorbing more than 10 per cent. of its weight of moisture when exposed in a dry state to the air. A weighed quantity of the substance was heated on the water-bath with a known volume of standard potassium dichromate and sulphuric acid, and at the end of two days the unreduced chromic

acid was estimated. Considerably less chromic acid was used than would have been the case if the whole of the tin had been in the stannous condition, and it was clear that the substance was either a mixture of the hydrated stannous and stannic oxides or possibly contained an intermediate oxide, the lower oxide or oxides constituting at least three-fourths of the total. This substance was not soluble in water even on heating on the water-bath for some days. On evaporating the brown liquid in the dialyser, no separation or gelatinisation occurred until it was almost completely evaporated to dryness. The gelatinous matter which separated at this point was readily soluble in water, giving a clear solution, but when once it had been evaporated to dryness, the residue was completely insoluble. Although not identical in quantitative composition, it is no doubt essentially the same qualitatively as the product produced by precipitation with calcium chloride and other electrolytes. The brown liquid in the experimental bottles was found to contain 0.063 gram of tin per c.c., whilst the colourless liquid contained only 0.006 gram of tin per c.c. On passing hydrogen sulphide into the coloured solution the colour changed to a very dark brown, but no precipitation occurred. On adding a few drops of hydrochloric acid, however, a dark brown precipitate of sulphide at once formed. The addition of hydrogen sulphide to the colourless liquid from the bottles caused an immediate precipitation. In the next place, it was decided to study the behaviour of the pure crystallised stannous tartrate towards water and tartaric acid solutions. On heating stannous tartrate crystals with water, decomposition occurs, a colourless, opalescent liquid being formed, which remains opalescent even when filtered through papers of the closest texture. On passing hydrogen sulphide through this liquid, no precipitation is formed, but a deep brown liquid having a greenish fluorescence results. The liquid itself was strongly acid to litmus, and evidently consisted of tartaric acid and colloidal stannous hydroxide resulting from the hydrolytic dissociation of the tartrate. The solid stannous tartrate was next heated with 1 per cent., 2 per cent., and 5 per cent. solutions of tartaric acid. At first no action appeared to take place, and after heating on the water-bath for six hours, little more than a trace of the tartrate had dissolved. The clear, supernatant liquid gave an immediate slight brown precipitate, showing that a little tin had passed into solution, but that no colloid had formed. On continuing the heating for several days, it was observed that the tartrate dissolved slowly, and that the liquid, which was, of course, originally colourless, gradually acquired a deep brownish-yellow colour with a greenish fluorescence, and closely resembled in appearance the contents of certain of the experimental bottles. On

passing hydrogen sulphide into this liquid, no precipitation occurred, but a deep brown coloration, characteristic of colloidal stannous sulphide, resulted. On continuing the heating for a further period of six days, it was noticed that the orange colour of the solution disappeared, giving place to a bluish-white, opalescent liquid. This gave no precipitate with hydrogen sulphide, but only a light yellow coloration. On the addition of a drop of hydrochloric acid, a yellow precipitate of stannic sulphide (probably with some oxide) at once formed. On heating some of the crystallised stannous tartrate with a 5 per cent. solution of tartaric acid in a sealed tube, no change was observed, although the heating was continued for several weeks.

As these experiments appeared to throw a great deal of light on the nature of the reactions occurring in the experimental bottles, it was decided to heat some of the orange-brown liquid from one of the bottles on the water-bath with free exposure to air. At first the colour deepened slightly, and then gradually became fainter, until at the end of a week a bluish-white, opalescent liquid remained, precisely similar in appearance to that obtained in the above experiment with the stannous tartrate. A small quantity of a colourless, transparent jelly separated, which doubtless consisted of the gel of colloidal hydrated stannic oxide. This liquid gave only a yellow coloration with hydrogen sulphide, but on the addition of a drop of hydrochloric acid, a copious precipitate formed. On adding a drop of hydrochloric acid to the colourless, opalescent liquid, a gelatinous precipitate formed which dissolved in an excess of the acid. The liquid evidently consisted therefore of a colloidal solution of hydrated stannic oxide, produced from the coloured solution by atmospheric oxidation. On adding a little hydrated stannous oxide to the colourless solution, the orange-brown colour returned.

In the light of the results of these experiments, I think the reactions occurring in the experimental bottles can be completely explained. Certain of the bottles had by chance (for at the time I attributed no importance to this point) been closed with well-fitting corks, and consequently the only oxygen available was that contained in the few c.c. of air above the liquid. In these, practically no action occurred, the tin remaining quite bright, or, at the most, exhibiting an etched appearance. In others, however, owing chiefly to the fact that the tin rods were not quite round, and so did not tightly close the holes bored through the corks, air could enter so soon as a reduction of pressure, due to the union of oxygen with the metal, occurred within the bottles. A very gradual supply of oxygen was thus maintained, in a manner which could



not have been improved upon if the experiment had been specially devised for the purpose. It is quite clear that under the influence of the tartaric acid the tin is readily attacked by oxygen, with the formation of stannous tartrate. Under the conditions of the experiment this probably, in the course of time, forms supersaturated solutions, from which the tartrate slowly crystallises, usually on the surface of the tin, but occasionally on the surface of the glass. The tartrate so formed undergoes dissociation, and the resulting stannous hydroxide, in the presence of the very limited supply of air, undergoes slow oxidation with the formation of the coloured compound above mentioned. Owing to the fact that only a very small quantity of oxygen was able to obtain access to the contents of the bottles, and that this would have to serve the double purpose of oxidising the tin and of oxidising the stannous salt formed, this coloured compound escaped conversion into the colourless stannic compound, which would undoubtedly have taken place if there had been free access of air or less tin. Owing to the great purity of the stannous tartrate formed under these conditions—that is to say, to the absence of electrolytes—the resulting colloidal solutions exhibited a high degree of stability, and, as will be seen by reference to the numbers given above, attained a considerable strength. Incidentally, it will be seen that these results are opposed to the statement of Bonquet (*J. Pharm. Chim.*, 1817, **11**, 459), that stannous tartrate dissolves in hot water without decomposition. Several observers have called attention to the formation of a dark coloured compound intermediate between stannous and stannic oxide, the compound having been first referred to by Frémy in 1844, who obtained a reddish-coloured powder by adding metastannic acid to a solution of stannous chloride, but, so far as I am aware, it has not been hitherto obtained by direct oxidation of the lower oxide. This coloured compound has been regarded as a compound of the two oxides, but the above mode of formation rather tends to support the view that it may be the hydrated sesquioxide, the existence of which is very probable, on theoretical grounds, and which receives further support from the fact that the existence of tin triethyl has been definitely established by Rügheimer (*Linnæus*, 1908, **364**, 51). As against the view that the coloured substance is a molecular compound of stannous and stannic oxide, the following experiment may be instanced.

Solutions were prepared containing stannous sulphate, ammonium persulphate, and quantities of sulphuric acid, varying from 1 to 20 per cent. These solutions were allowed to remain, and at the end of some weeks it was found that in all cases a certain amount

of colour had developed, the colour being deepest in the solutions containing the largest proportions of sulphuric acid. Under these conditions it is almost inconceivable that any compound, such as stannous stannate, should be capable of existing. Attempts have been made to isolate the intermediate oxide and to prepare salts corresponding with it, but up to the present without success. This work is being continued. Mr. Emil Hatschek, who has been kind enough to examine the coloured colloidal solution ultra-microscopically, reports as follows:

"For the purpose of ultra-microscopic examination, the solution was diluted to fifty times its volume, and the dilute solution was examined with the Jentzsch and the Reichert ultra-condensers. On diluting the solution with tap water, it became turbid, and showed an enormous number of submicrons. The solution accordingly appears to undergo coagulation by the small amount of electrolytes present in tap water, and thus exhibits a sensitiveness not usually found in the classical stannic acid solutions, but characteristic of certain solutions of aluminium hydroxide.

"If distilled water is used, the dilute solution is perfectly clear and stable. In the ultra-microscope it shows a small number of particles, probably due to incipient coagulation by carbon dioxide contained in the distilled water. The solution, like the known solutions of stannic acid and practically all solutions of metallic hydroxides, is therefore also an emulsoid solution."

My best thanks are due to my assistant, Dr. E. Wechsler, for valuable assistance in connexion with this work.

### LXXIX.—*Some Double Salts with Acetone or Crystallisation and the Crystallisation of Silver Iodide, Silver Bromide, and Cuprous Iodide.*

By JAMES ERNEST MARSH and WILLIAM CLAUDE RHYMES.

IN 1910 (T. 97. 2297) some liquid ether compounds of double halogen salts were described, which were chiefly mercury compounds, but silver iodide, cuprous iodide, and lead iodide were found to give liquid compounds with lithium iodide and ether. In the present paper a complete series of crystalline double salts of silver iodide with the alkali-metal iodides is described. These salts are of the type  $M_1,2AgI$ . Evidence is also given of the existence of salts of the type  $M_1,3AgI$ , and of salts containing less than  $2AgI$ .

We have also made, but have not completed the examination of, a series of double cuprous iodides. It was found that when the ethereal solution of lithium silver iodide (*loc. cit.*, p. 2308) was allowed to evaporate, crystals of silver iodide were deposited, and that these crystals, together with the deliquesced lithium iodide, were soluble in acetone, and crystallised out again on evaporation of the acetone. In a similar way, silver bromide and cuprous iodide have also been obtained in the crystalline state.

The salts described in this paper were obtained by crystallisation from acetone, and most of them contain acetone of crystallisation. They lose this acetone with great rapidity on exposure to the air, and either effloresce and crumble to powder or deliquesce. The determination of the acetone of crystallisation thus presented considerable difficulty. The method which was in general adopted is as follows: The double salt with some excess of solvent was contained in a Liebig drying tube; a current of dry air was passed through the tube until the excess of solvent was removed; acetone vapour was then passed through the tube until the crystals began to liquefy; then dry air was passed until the crystals were just dry. The method, perhaps, does not lend itself to extreme accuracy, but it gave fairly consistent results. The lithium, sodium, ammonium, and potassium double silver salts deliquesce in contact with acetone vapour under these conditions; the rubidium and cesium salts do not.

*Cesium Silver Iodide, CsI<sub>2</sub>AgI.*

This is the only salt of the series which does not take up acetone of crystallisation. It is more soluble in cold than in hot solution, differing in this also from the other salts. It is also much the least soluble. It was obtained by dissolving a mixture of cesium and silver iodides in the molecular proportion of 1 to 2 in 20 to 30 times its weight of acetone cooled with ice and salt. The solution was filtered from a little sediment, and crystallised by evaporation of the acetone. If the solution is warmed, the salt is precipitated, but not in good crystals. On evaporation the salt separates in long, hair-like crystals, which are colourless and double refracting with straight extinction. They remain colourless up to their melting point at about 210°. The fusion is yellow, and quickly separates a yellow solid, probably silver iodide. The crystals are free from acetone, and are stable in the air. They do not absorb acetone or water vapour, but when placed in water decompose with separation of silver iodide. The crystals lost less than 0.3 per cent. of their weight on heating, and were therefore free from acetone and water.

Found, AgI = 63.9.

CsI<sub>2</sub>AgI requires AgI = 61.1 per cent.

*Rubidium Silver Iodide*,  $\text{RbI}, 2\text{AgI}, 2\text{C}_3\text{H}_6\text{O}$ .

This salt is obtained when rubidium iodide and silver iodide are dissolved in acetone, and the solution evaporated in dry air.

It is extremely soluble in the solvent, and a hot, strong, saturated solution crystallises on cooling. The crystals were obtained in transparent, colourless needles, double refracting, with straight extinction; on exposure to the air they lose their acetone and crumble to powder. The dry salt does not deliquesce, but absorbs water slightly from the air:

Found,  $\text{C}_3\text{H}_6\text{O} = 14.8$ .

$\text{RbI}, 2\text{AgI}, 2\text{C}_3\text{H}_6\text{O}$  requires  $\text{C}_3\text{H}_6\text{O} = 14.5$  per cent.

Found (in dried salt)  $\text{AgI} = 68.67$ .

$\text{RbI}, 2\text{AgI}$  requires  $\text{AgI} = 68.9$  per cent.

Rubidium iodide does not appear to form a double salt with silver iodide in equal molecular proportions, or, at any rate, the compound  $\text{RbI}, \text{AgI}^*$  is not soluble in acetone at the ordinary temperature. Some of the rubidium iodide is left undissolved. More of it, however, is dissolved than corresponds with the formula  $\text{RbI}, 2\text{AgI}$ . Since rubidium iodide and silver iodide separately are scarcely at all soluble in acetone, another double salt, containing a larger amount of rubidium iodide, is perhaps indicated possibly  $2\text{RbI}, 3\text{AgI}$ . A salt with excess of silver iodide, of the formula  $\text{RbI}, 3\text{AgI}$ , is also indicated, but has not been analysed. It was noticed, when dissolving the salts in the proportion 1 : 2, that the silver iodide dissolved before the rubidium iodide, and on addition of another molecular proportion of silver iodide it dissolved when the liquid was cooled. A little below  $0^\circ$ , the whole solution froze to a hard, solid mass.

*Potassium Silver Iodide*,  $\text{KI}, 2\text{AgI}, 2\text{C}_3\text{H}_6\text{O}$ .

The potassium salt was obtained in the same way as the rubidium salt, and gave crystals closely resembling the latter in appearance:

Found,  $\text{C}_3\text{H}_6\text{O} = 16.36$ .

$\text{KI}, 2\text{AgI}, 2\text{C}_3\text{H}_6\text{O}$  requires  $\text{C}_3\text{H}_6\text{O} = 15.4$  per cent.

The result is perhaps as accurate as one could expect from the slight hold the salt has on its acetone of crystallisation:

Found (in dried salt),  $\text{KI} = 25.5$ .

$\text{KI}, 2\text{AgI}$  requires  $\text{KI} = 26.1$  per cent.

The salt on exposure to the air loses its transparency with loss of acetone. The acetone-free salt takes up water from the air

\* The salt  $\text{RbI}, \text{AgI}$  has since been obtained by crystallisation from a mixture of acetone and water.

without deliquescing. Like the rubidium salt, a solution can be obtained in acetone of potassium and silver iodides in the proportion of KI to 3AgI. In a freezing mixture of ice and salt, the solution, if not too diluted, freezes to a solid mass. When warmed, the solution deposits some of the silver iodide in the amorphous form.

Potassium and silver iodides dissolve in acetone also in the proportion of KI to AgI. On evaporation of the acetone, crystals are left which deliquesce in moist air, forming a solution from which crystals of silver iodide eventually separate. Potassium silver iodide,  $\text{KI}_2\text{AgI}$ , is soluble in other ketones, such as methyl ethyl ketone, which gives a solution of a deep orange colour. Diethyl ketone also dissolves it, but not quite completely, and possibly some decomposition occurs. The solution in diethyl ketone, like that in acetone, is nearly colourless.

*Sodium Silver Iodide,  $\text{NaI}_2\text{AgI} \cdot 3\text{C}_2\text{H}_5\text{O}$ .*

This salt forms colourless, transparent, needle-shaped crystals, double refracting, with straight extinction.

It is extremely soluble in acetone, and on evaporation of the acetone a jelly-like mass is left, in which the crystals gradually form:

Found,  $\text{C}_2\text{H}_5\text{O} = 21.59$ .

$\text{NaI}_2\text{AgI} \cdot 3\text{C}_2\text{H}_5\text{O}$  requires  $\text{C}_2\text{H}_5\text{O} = 21.91$  per cent.

Found (in dried salt),  $\text{AgI} = 76.1$ .

$\text{NaI}_2\text{AgI}$  requires  $\text{AgI} = 75.8$  per cent.

Sodium and silver iodides dissolve in acetone in equal molecular proportions, but the crystals on evaporation do not appear to be homogeneous. Nor has the phenomenon of solution in these proportions the same significance as the solution of the salt  $\text{KI}_2\text{AgI}$ , since sodium iodide by itself is readily soluble in acetone.

*Lithium Silver Iodide.*

This salt crystallised well from dry acetone in colourless needles, with strong double refraction and straight extinction.

The determination of the acetone of crystallisation did not give very concordant results, the amount varying between three and four molecules. The salt does not crystallise out at all when the solution is allowed to evaporate exposed to the air. The crystals are obtained by evaporating the acetone in a current of dry air. When the acetone solution is exposed to the atmosphere crystals of silver iodide are gradually formed. This phenomenon is referred to again later.

*Ammonium Silver Iodide,  $\text{NH}_4\text{I} \cdot 2\text{AgI} \cdot 3\text{C}_3\text{H}_7\text{O}$ .*

This salt crystallises well from acetone in colourless needles, double refracting, with straight extinction. We have not at present sufficient crystallographic evidence to determine whether the crystalline form of this salt is different from that of the potassium salt.

Found,  $\text{C}_3\text{H}_7\text{O} = 21.8$ .

$\text{NH}_4\text{I} \cdot 2\text{AgI} \cdot 3\text{C}_3\text{H}_7\text{O}$  requires  $\text{C}_3\text{H}_7\text{O} = 22.0$  per cent.

Found (in dried salt),  $\text{AgI} = 77.0$ .

$\text{NH}_4\text{I} \cdot 2\text{AgI}$  requires  $\text{AgI} = 76.4$  per cent.

An ethylamine hydriodide-silver iodide was also crystallised from acetone, and resembled the ammonium salt in general appearance. There seems to be no doubt that a whole series of organic compounds of this type are capable of existing.

*Crystallised Silver Iodide.*

When a solution of silver iodide in lithium iodide and acetone is exposed to the air, after some days crystals of silver iodide begin to form and grow in the solution. The crystals are of the hexagonal form and transparent, and there seems to be no difficulty in obtaining crystals in this way of any desired size. Silver chloride also dissolves in an acetone solution of lithium iodide, and silver iodide crystallises from the solution. These crystals were analysed by conversion into silver chloride in a current of chlorine. As the iodine is displaced by the chlorine, the crystals crumble to powder without heat being applied to them:

0.6120 gave 0.3716  $\text{AgCl}$ .  $\text{Ag} = 45.7$ .

$\text{AgI}$  requires  $\text{Ag} = 45.9$  per cent.

*Crystallised Silver Bromide.*

Lithium bromide and silver bromide dissolve fairly well in acetone, in the proportions of  $\text{LiBr}$  to  $2\text{AgBr}$ . Like cesium silver iodide, the solubility is greatest in the cold solution. As the temperature is allowed to rise, silver bromide crystallises out in large, flat, yellow, transparent plates, which are very tough and flexible. To obtain good crystals, the acetone should be pure, that obtained from bisulphite being the best. The crystals lost 1.22 per cent. of their weight on heating, which is probably due to included solvent:

1.0269 gave 0.7718  $\text{AgCl}$ .  $\text{Ag} = 57.2$ .\*

$\text{AgBr}$  requires  $\text{Ag} = 57.4$  per cent.

\* Allowance is made for 1.22 per cent. of volatile impurity.

*Double Cuprous Salts and Crystalline Cuprous Iodide.*

Cuprous iodide is readily soluble in acetone in the presence of an alkali-metal iodide. Sodium iodide and cuprous iodide dissolve in acetone in the proportions of  $\text{NaI}$  to  $2\text{CuI}$ . On evaporation, a well-crystallised salt is obtained. Lithium iodide and cuprous iodide also dissolve in acetone in about the same relative proportions. On slow evaporation in the air cuprous iodide crystallised out. The crystals are fairly large and colourless, but opaque.

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# LXXX.—Notes on the Determination of the Electrical Conductivity of Solutions.

By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

IN a series of experiments preliminary to the determination of the temperature coefficients of the electrical conductivity of dilute salt solutions, the resistance of a solution was measured both with a commutator of the pattern described by Whetham (*Phil. Trans.*, 1900, A, **194**, 321) and with a telephone and induction coil. As the latter method appeared to give a lower value for the resistance, a careful comparison of the two methods has been made. The results show that they do not yield the same value for the resistance, and that the ratio of the resistances found by them varies (1) with the construction of the commutator, (2) with the rate at which the commutator is driven, (3) with the magnitude of the resistance to be measured, (4) with the form of the cell.

In the course of the work a new form of conductivity cell was devised for use with dilute solutions, which possessed several advantages over the usual patterns, and has since been found most useful in the investigation of both aqueous and non-aqueous solutions.

## Comparison of the Values found for the Electrical Resistance of a Solution by the Commutator and Telephone Methods.

The resistance of solutions of potassium chloride (approx. 0.001N) was measured between three pairs of platinum plates: (a) a pair of small plates (area 2.5 sq. cm.) coated with platinum black, and plated close together in a cell of the Arrhenius pattern; and (b) and (c) two separate pairs of platinum plates of a larger size (area 6 sq. cm.) coated with grey platinum obtained by heating platinum

black to dull redness (Whetham, *loc. cit.*, p. 329) in a large cell containing 1500 c.c. of solution. The solutions being so dilute, special precautions were taken to protect them from contamination with impurities during the measurements, and the resistance of the solutions was tested at the end of each experiment by the method in use at the beginning, in order to see that it had not varied.

In the first set of experiments the results obtained with a double pole Bell telephone of the ordinary pattern and a small induction coil were compared with those obtained with a rotating commutator with eight sectors and insulated strips separating each pair. The commutator was driven by a small motor, and the speed was altered by varying the resistance in the motor circuit. A Nalder galvanometer was used as a current detector. The bridge consisted of three metres of wire wound on a marble drum, with extensions which increased its effective length to 30 metres. An accumulator was used as the source of current with the rotating commutator, a resistance of 2000 ohms being placed in the battery circuit.

TABLE I.  
*Resistances in Ohms.*

Electrodes.	By telephone.	By commutator.			
		High speed.	Low speed.		
A. Black Pt ...	$\bar{E}_1$ 237.51	$\bar{E}_2$ 238.77	$\bar{E}_3$ 238.60	$\bar{E}_4, \bar{E}_5$ 1.0053	$\bar{E}_6, \bar{E}_7$ 1.0016
B. Grey Pt ...	1391.6	1401.2	1399.4	1.0049	1.0056
C. „ Pt ...	2264.7	2277.6	2271.3	1.0057	1.0042

These results show that the telephone gives a lower value for the resistance than the commutator, and that the value of the resistance found by the latter depends to a small extent on the rate at which the commutator is driven. An increase of speed, that is, an increase in the number of alternations per minute and a decrease in the length of time during which a direct current flows through the solution, leads to a lower value for the resistance.

In some further experiments, in which the largest resistance measured was 2200 ohms, it was found (1) that if the electrolytic resistance is measured by a telephone and induction coil, the result is independent of the note the telephone is giving, and does not vary with different telephones and coils, and (2) that if two wire resistances not exceeding 4000 ohms are compared with a rotating commutator, the result is independent of the rate at which the commutator is driven, and is identical with the result obtained with a telephone.



A further comparison was made with the same pairs of electrodes in solutions of potassium chloride of nearly the same strength by three independent observers (Mr. T. S. Moore and the authors), in order to eliminate the effect of personal error; individual results never differed from one another by more than five parts in ten thousand, and usually agreed more closely. To increase the value of the comparison, a different pattern of commutator, kindly lent by Mr. B. Lambert, was also used. It was made with only two sectors. The number of alternations was determined by means of a revolution counter. The resistance in the battery circuit in all the commutator measurements was 700 ohms. The results are given in the following tables:

TABLE II.  
*Resistances in Ohms.*

	By telephone, $r_1$ .	By commutator (two sectors).		By commutator (eight sectors).			
		2200 alts. $r_2$ .	2750 alts. $r_3$ .	2640 alts. $r_4$ .	3200 alts. $r_5$ .	5700 alts. $r_6$ .	6500 alts. $r_7$ .
A.	236.94	238.65	238.60	238.24	—	—	237.74
B.	1388.6	1400.6	1399.0	1395.6	1394.8	1394.0	1392.2
C.	2260.9	2277.5	2275.6	2271.4	—	—	2266.2

*Ratios of Resistances Determined by Telephone and Commutator.*

	$r_2/r_1$ .	$r_3/r_1$ .	$r_4/r_1$ .	$r_5/r_1$ .	$r_6/r_1$ .	$r_7/r_1$ .
A.	1.0072	1.0074	1.0055	—	—	1.0051
B.	1.0086	1.0075	1.0050	1.0015	1.0039	1.0026
C.	1.0073	1.0065	1.0046	—	—	1.0023

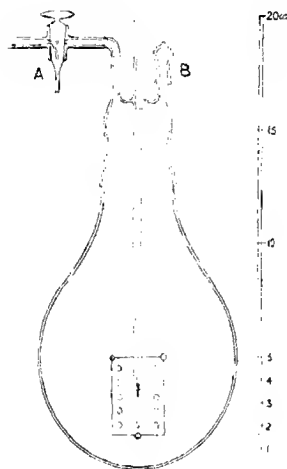
These results agree with those obtained in the preliminary series. Using the eight sector commutator at 2600 revolutions per minute, the resistance with each kind of plate is, roughly, 0.5 per cent. higher than that found with the telephone. As the number of revolutions increases, the resistance appears to diminish, and its value approaches that found with the telephone. The higher the resistance the more closely does the resistance measured by the commutator agree with that found by the telephone. However, in some later experiments with Mr. Bourdillon, when higher electrolytic resistances (up to 250,000 ohms) were measured by both methods, large differences, amounting in some cases to 5 per cent. were observed.

#### *Conductivity Cell for Use with Dilute Solutions.*

\* In order to determine the conductivity of aqueous solutions more dilute than 0.001*N*, when the conductivity of the solvent under the best conditions amounts to 1 or 2 per cent. of the conductivity of

the whole solution, it is necessary to start with a considerable quantity of the solvent (compare Whetham, *loc. cit.*; Kohlrausch and Maltby, *Wiss. Abh. Phys. Tech. Reichsanstalt*, **3**, 157) in a cell which protects it from contamination with the air, and to add to it from weight- or volume-pipettes successive small quantities of a solution of the electrolyte under examination.

It must be possible to make these additions and to stir the contents of the cell without any risk of introducing impurities from the air. These conditions are fulfilled by the cell shown in the figure. It is made entirely of boro-silicate glass, and holds about 300 c.c. of solution. The tubes carrying the platinum are fused through



the cap of the cell, and the electrodes are held firmly together by small rods of glass fused on at the corners. They are covered with grey platinum (obtained by heating platinum black to redness) to avoid occlusion by platinum black (compare Whetham, *loc. cit.*, p. 329). The water or solution can be stirred by rotating the cap of the cell; the holes in the electrodes shown in the figure ensure the stirring of the solution between the plates even when they are within a few mm. of one another. The tap A admits a current of air freed from carbon dioxide and ammonia by passing through sulphuric acid and over soda-lime, and then through water to saturate it with water vapour.

At the beginning of an experiment the cell is cleaned with

conductivity water and dried, and a current of purified air passed through for some minutes. It is then weighed, and conductivity water is run in through the opening *B* until the surface reaches an etched mark on the cell. The mark is placed at such a height above the electrodes that the cell constant does not vary when small quantities of solution are added to the solvent. The cell is then weighed again to ascertain the weight of water it contains, and put into the thermostat. The water is stirred, and its resistance measured from time to time. Any change in the resistance that may have taken place after the temperature of the water has reached the temperature of the bath is due either to the solubility of the glass, to the solution of electrolytes absorbed by the electrodes, or to the exchange of volatile impurities with the air in contact with the water. If the resistance is falling, it is a good plan to pass in a little purified air, the cap at *B* being removed for a few seconds; this will often stop the fall and cause the resistance to rise. When the resistance of the solvent water is steady, small measured quantities of a solution of the electrolyte to be studied are run in from a weight- or volume-pipette, a slow current of purified air being admitted at *A* so as to prevent atmospheric impurities from entering the cell while the addition of solution is being made.

The following series of measurements show that the constancy of the solvent resistance can be maintained for a considerable time with water which has a specific conductivity of approximately 1 gemmho ( $1 \times 10^{-6}$  reciprocal ohms).

Time, hrs. mins.	Resistance, in ohms.	Time, hrs. mins.	Resistance, in ohms.
— —	30400	19 —	30800
— 20	30500	19 30	30800 X
— 22	30500 X	20 —	30700
— 25	30500	21 —	30600 X
— 28	30600	22 —	30600 X
— 30	30600	23 —	30500

At points marked X the cap *B* was removed, and a slow current of air admitted at *A*, in order to show that portions of solution could be added without changing the resistance of the solvent.

Using water with a conductivity as low as 0.11 gemmho. Mr. Bourdillon found that the average rise per hour was 0.004 gemmho when the electrodes had not been in contact with a salt solution for some time, and 0.01 gemmho when they had been soaked for twelve hours in pure water after use with 0.05*N*-solution of potassium chloride.

In order to allow the cap of the cell to rotate easily and to ensure good stirring, the ground joint is lubricated with a little vaseline

previously purified by being heated with conductivity water to remove traces of organic acids. Care must be taken always to set the cap of the cell in the same position; for this purpose marks are etched on the edge of the cap and on the neck of the flask, and these are brought into coincidence. Since the cap is ground on outside the neck of the flask, there is no fear of dust falling in while the cap is being rotated.

The authors have pleasure in acknowledging their indebtedness to a grant from the Research Fund of the Royal Society, from which much of the cost of the apparatus used in this work was defrayed.

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### LXXXI.—*The Preparation of Conductivity Water.*

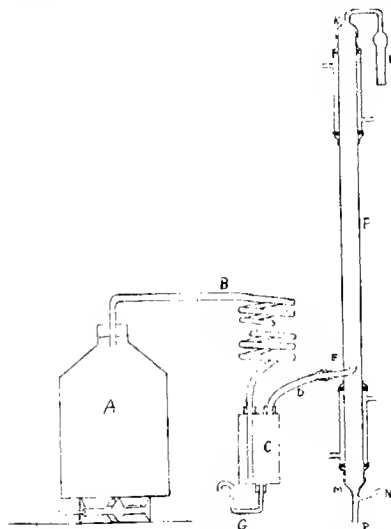
By ROBERT BOURDILLON.

HITHERTO most work on the conductivity of dilute solutions has been done with water possessing an electrical conductivity of at least 0.7 gemmho ( $0.7 \times 10^{-6}$  reciprocal ohms). The use of such water involves a correction for solvent conductivity which may amount to 8 per cent. or more in  $N/10,000$ -solution; since this correction is uncertain for salt solutions, and leads to most anomalous results for solutions of dilute acids, it is obviously important to reduce it as far as possible.

This paper describes a still which will deliver 7 or 8 litres of water of conductivity below 0.2 gemmho in a single distillation from Oxford tap water. It is also found that in a suitable air-tight cell such water can be kept with only a very slow rise in conductivity.

The boiler .1 (see diagram) is of copper and holds about 13 litres. It is closed by a rubber cork, through which passes a copper tube *B* (1.3 cm. external diameter, 8.5 metres long) coiled into a spiral of 19 turns. This spiral forms an efficient trap for spray, and its lower end is fixed by a rubber cork into a copper cylinder *C*. *B* and *C* are jacketed with cotton waste and boiler felt, but about one-fifth of the steam from the boiler is condensed here; this waste water escapes by the glass tube *G*, which is joined to *C* by a rubber cork, and bent as shown in the diagram in order to prevent the escape of steam. The steam passing through *B* and *C* goes up the

glass tube *D*\* into the condenser at *E*. The condenser is a long, vertical tin tube *F* (2.5 cm. internal diameter, 145 cm. long), with a narrow side-tube *E* soldered in with pure tin 45 cm. from the bottom, and turned upwards inside *F*. *F* is surrounded near the top and bottom by glass tubes through which cold water is passed, and is closed at the top by a glass cap *K*, which is affixed by a rubber ring and is connected with the air by a soda-lime tube *L*, and at the bottom by a glass cap *M*, carrying a side-tube *N*, and



joined by rubber tubing at *P* to the vessel in which the distilled water is to be collected. *K* and *M* might with advantage be made of tin, and soldered to *F* with tin. A continuous current of purified air (usually 3—3.5 litres per hour) enters at *N*, and passes out at *L*. It is purified by passing through glass spirals containing concentrated sulphuric acid and potassium hydroxide solution, and then through a long soda-lime tube. The continuous current of water was obtained by allowing a slow stream of water to fall down a vertical glass tube after the manner of a Sprengel pump; the tube

\* The tube *D* is joined to *C* by a rubber cork, and to *E* by a short piece of rubber tube; it is unnecessary, and is included in the author's still only because of the position in the laboratory in which the still is placed. It would be better to attach *E* directly to *C*.

was connected at the bottom to a large bottle, from which the water and air were allowed to escape by separate outlets.

The boiler is filled with tap water, to which about 5 grams of potassium hydrogen sulphate have been added. When boiling begins, the greater part of the carbon dioxide is expelled rapidly, and the ammonia is retained. The steam passes through *B* and *C*, and leaves the tube *E* with a considerable upward velocity (as may be seen by removing the cap *K*). On reaching the part of *F* which is surrounded by the top cooling tube, it condenses, and the water thus formed trickles down past a long column of steam and purified air, which apparently removes the volatile impurities. The object of the lower cooling tube is to cool this water to any desired temperature before it leaves the condenser, and very little water is condensed here.\* It is most important to keep all connexions airtight; the work was done in a cellar without good ventilation, and it was found that any leak in the apparatus produced a large rise in the conductivity of the water.

If the distillation is carried on fairly fast (1.2 litres per hour), the conductivity of the resulting water falls rapidly, and remains below 0.13 gemmho after one litre has been collected. It is found advisable to stop the distillation when two or three litres are left in the boiler, in order to prevent incrustation from calcium sulphate. The following table shows the average course of a distillation, and was obtained by attaching a conductivity cell directly to the condenser.

Time in minutes from beginning of distillation.	Conductivity in gemmhos at 18°.	Total volume of distillate in c.c.
7	4.2	109
10	1.4	179
13	0.91	249
15	0.48	319
18	0.25	385
21	0.15	460
24	0.14	530
27	0.11	600
30	0.11	670
1 hr. 15 min.	0.11	about 6000

From the first half hour until the distillation is stopped, the values found vary from 0.11 to below 0.09 gemmho, occasionally rising to 0.12.

The values given above are only approximate, and may contain an error of 10 per cent., but they are confirmed by a number of observations made with the cell described below. The lowest value

\* The top cooling tube needs a rapid stream of cold water, the bottom tube needs much less; in order to cool the distilled water to any desired temperature, it is best to connect the two tubes to separate water taps.

observed in this cell was 0.086 gemmho at 18°, but there are indications that the conductivity of the water at the mouth of the condenser falls below this. The lowest value obtained by Kohlrausch and Heydweiller by distillation in a vacuum was 0.04 gemmho at 18°.

If phosphoric acid is used in the boiler instead of potassium hydrogen sulphate, very similar results are obtained. If no chemicals are used, a large quantity of mediocre water is obtained, the conductivity falling to 0.3 gemmho about two hours after distillation begins, and only falling to 0.17 gemmho after 4.5 hours' distillation. If distilled water is used instead of tap water and potassium hydrogen sulphate is added, slightly better water is obtained, but there is little difference, and the conductivity of the product does not fall much below 0.09 gemmho. If tap water is distilled with potassium hydrogen sulphate but no pure air is passed up the condenser, the conductivity of the product falls to about 0.25 gemmho after some hours, but does not fall below this value. A few trials were made with a condenser similar in form to that described above, but only 46 cm. long and 2 cm. internal diameter, but no water was obtained of a conductivity of less than 0.23 gemmho.

*Behaviour in Conductivity Cell.*—Nothing is gained by using such water in a conductivity cell that is not air-tight. Hartley and Barrett (this vol., p. 788) have devised a cell which is very convenient, as its contents can be stirred and fresh solution can be added without risk of contamination from the air. It is made of borosilicate glass, and if its electrodes have been soaked in water for a long time, and it is then filled with purified air, water with a conductivity of 0.11 gemmho increases its conductivity by about 0.02 gemmho during the first hour after it is placed in the cell, and during the second and subsequent hours the rise is only 0.004 or 0.003 gemmho per hour. If the cell has contained  $N/20$ -potassium chloride solution, and has then been thoroughly washed and left to soak for one night with pure water in it, the rise during the first hour is about 0.03 gemmho, and that during the next few hours is about 0.01 gemmho per hour. An alteration of 0.05 gemmho in the conductivity of the solvent would change the apparent conductivity of  $N/10,000$ -potassium chloride solution by about 0.03 per cent. Since it is easy to take measurements of a solution within half an hour of the determination of its solvent conductivity, it is evident that the alteration in the solvent is so small that a correction for it can be made safely, even in very accurate work.

As yet only a few attempts have been made to keep water of low conductivity for any length of time. It was found that, on

collecting and storing water in 3-litre Jena-glass flasks fitted with siphon outlet tubes, and with air inlets protected by soda-lime tubes, the conductivity rose from 0.12 gemmho, when first collected, to 0.2 gemmho in two or three days, and to 0.4 or 0.45 gemmho in two or three weeks. It can be kept for a month or two without its conductivity rising above 0.5 gemmho.

In conclusion I should like to express my thanks to Mr. Hartley for much valuable advice and help. The cost of the measuring apparatus used in this research was defrayed by a grant from the Government Grant Committee of the Royal Society, made to Mr. Hartley for the investigation of the conductivity of dilute aqueous solutions.

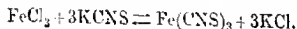
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## LXXXII.—The Reaction between Ferric Salts and Thiocyanates.

By JAMES CHARLES PHILIP and ARTHUR BRAMLEY.

This reaction has been the subject of numerous investigations, many of them carried out with the object of applying the law of mass action to the equilibrium which is established between the various substances concerned, and which is generally represented as follows:



The displacement of equilibrium which results from change of concentration or temperature has been deduced from the corresponding changes in the colour intensity (see Gladstone, *Phil. Trans.*, 1855, **145**, 179; Kriess and Moralt, *Annalen*, 1890, **260**, 193; Magnanini, *Zeitsch. physikal. Chem.*, 1891, **8**, 1; Vernon, *Chem. News*, 1892, **66**, 177, 191, 202, 214; 1893, **67**, 66; Gladstone, *ibid.*, 1893, **67**, 1; Rosenheim and Cohn, *Zeitsch. anorg. Chem.*, 1901, **27**, 280).

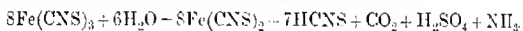
There is, however, one fact which has a very definite bearing on the relation between ferric salts and thiocyanates, and to which too little attention has been paid, although it has been observed by a number of workers. This fact is the gradual diminution in the intensity of colour which takes place in a given solution of ferric thiocyanate (see, for instance, Vernon, *loc. cit.*; Oerum, *Zeitsch. anal. Chem.*, 1904, **43**, 152; Stokes and Cain, *J. Amer.*



*Chem. Soc.*, 1907, **29**, 412, 445). It has been noted by some investigators that this bleaching is associated with a reduction of the iron from the ferric to the ferrous condition (Stokes and Cain, *loc. cit.*, 412; compare Rosenheim and Cohn, *loc. cit.*; Tarugi, *Gazzetta*, 1904, **34**, ii, 326; Bongiovanni, *ibid.*, 1907, **37**, i, 472), but apparently there are no definite recorded data bearing either on the nature of the corresponding oxidation products, or on the velocity of the reduction and its variation with concentration, temperature, acidity, etc.

The fact that there is a progressive reduction of the iron in a ferric thiocyanate solution was discovered incidentally in the course of another investigation, and independently of the observations recorded by previous workers. It was then thought worth while to search for the oxidation products which must necessarily be formed in proportion as the iron is reduced.

Judging from the recorded action of common oxidising agents on thiocyanic acid, the authors expected to find that at least the main oxidation products would be hydrocyanic and sulphuric acids. Investigation showed, however, that at the ordinary temperature the carbon of the thiocyanate, so far as oxidation of this substance has taken place, appears, not as cyanide, but as carbon dioxide, whilst the corresponding sulphur is converted into sulphate. Quantitative comparison of the iron reduced on the one hand, and the carbon dioxide and sulphate formed on the other, has shown that for every 8 gram-atoms of iron reduced there are formed 1 gram-molecule of carbon dioxide and 1 gram-molecule of sulphuric acid. On the basis of these facts, the decomposition of ferric thiocyanate might be represented by the equation:



This equation, however, whilst consistent with the facts, so far as the formation of carbon dioxide and sulphuric acid is concerned, requires the production of ammonia to an extent beyond what is actually found. The quantity of ammonia obtainable from the reaction mixture is never more than about two-thirds of that required by the foregoing equation. The nitrogen therefore of the oxidised thiocyanate appears only partly as ammonia, and no definite information has been obtained as to the other product or products into which this element is converted.

The velocity of the reaction between ferric salts and thiocyanates presents various interesting features, although it has not been found possible to represent the course of the change by a mathematical formula. The study of mixtures containing a constant quantity of ferric salt and varying quantities of thiocyanate has shown that,

whilst at the start the reduction is slowest in those solutions with the least thiocyanate, it proceeds at a more even rate, until ultimately the extent of reduction is greatest in these cases. This peculiar behaviour is probably connected with the influence of acid, which retards the reduction where there is excess of thiocyanate, and slightly accelerates it where there is excess of iron. This observation is significant, since the progress of the reduction means the accumulation of acid and an increase in the relative concentration of thiocyanate.

#### EXPERIMENTAL.

##### *The Products of the Interaction of Ferric Salts and Thiocyanates.*

The fact that in a solution of ferric thiocyanate there is a gradual reduction of the iron was discovered incidentally in the process of standardising a solution of titanium trichloride. According to the method of standardisation proposed by Knecht and Hibbert, a solution containing a known amount of iron in the ferric condition, together with some mineral acid, is employed. A large excess of potassium thiocyanate is added as indicator, and the titanium trichloride is then run in until the red coloration due to ferric thiocyanate disappears entirely. In one standardisation portions of a prepared iron solution, with the added thiocyanate, had been heated before titration, and it was found that in these cases the volumes of titanium trichloride required varied in a very marked and irregular manner. Further examination showed that extensive reduction of the iron had taken place under the foregoing conditions. It was also observed that the iron was reduced to an appreciable, if much smaller, extent, even at the ordinary temperature, when the solutions containing ferric thiocyanate were allowed to remain some time before titration. For example, 10 c.c. of a solution containing about 6 grams of iron and 80 grams of ammonium thiocyanate per litre (that is,  $\text{Fe}:\text{NH}_4\text{CNS}=1:9$ ) required, when freshly prepared, 22.7 c.c. of the standard titanium solution. One hour later, 10 c.c. of the same mixture, which had been kept at  $25^\circ$ , required 20.1 c.c. of the titanium chloride solution. Hence about 10 per cent. of the iron had been reduced in this interval.

That a solution containing ferric thiocyanate undergoes a gradual change with time is clearly shown by the regular increase in the electrical conductivity of the solution. Such an increase was observed for a mixture of ferric ammonia alum and potassium thiocyanate, but was especially evident when the initial solution contained nothing but ferric thiocyanate. This was prepared by treating excess of freshly precipitated and well-washed ferric

hydroxide with a solution of thiocyanic acid. Table I contains a record of the relative values of the conductance ( $C$ ) at 25° of a ferric thiocyanate solution containing 9.6 grams of iron per litre.

TABLE I.

Time in hours.	Conductance $C$ .	Time in hours.	Conductance $C$ .
0.0	6.60	136.5	10.78
17.5	8.68	220.0	11.23
41.0	9.61	449.5	11.71
88.0	10.31		

This marked increase in conductivity is to be attributed to the production of new molecules, some of which at least must be largely ionised or yield ions of high mobility.

Obviously, in so far as the iron in ferric thiocyanate is reduced, there must be a corresponding oxidation of the thiocyanate. From analogy to what occurs when thiocyanates are treated with potassium permanganate, hydrogen peroxide, iodine, and hypochlorite, it was at first thought probable that the oxidation of the thiocyanate by ferric salt would lead to the formation of cyanide and sulphate. Many experiments, however, carried out with the object of detecting cyanide as one of the products of oxidation indicated that at the ordinary temperature cyanide was not formed to more than a very small extent, although at higher temperatures considerable quantities were produced. It was finally found, as already indicated, that the sulphur of the thiocyanate is oxidised to sulphate, and the carbon almost exclusively to carbon dioxide.

This result was established by the following quantitative experiments. A measured quantity of ferric salt solution of known strength was placed in a flask provided with a three-holed rubber stopper. Through two of these holes there passed glass tubes, one of which dipped into the solution and served for the admission of a current of nitrogen or air, free from carbon dioxide; the gas, after bubbling through the solution, passed on through the second tube referred to above. Through the third hole in the stopper there passed the stem of a dropping funnel, from which a measured quantity of potassium thiocyanate solution, of known strength, could be delivered. The current of nitrogen, after leaving the reaction vessel, passed in succession through (a) a solution of silver nitrate acidified with nitric acid, (b) distilled water, (c) a series of flasks containing measured quantities of standard baryta solution. The train of flasks was filled with nitrogen before the introduction of the baryta and the addition of the potassium thiocyanate solution to the ferric salt solution.

The experiment was started by running the potassium thiocyanate

solution into the ferric salt solution, and very shortly thereafter the formation of a white precipitate in the first baryta flask was observed. At the ordinary temperature the reaction was allowed to proceed for several days, after which, as shown by experiments described later, the change becomes very slow. By this time, a large quantity of precipitate had collected in the baryta flasks, whilst there was only a slight white deposit in the silver nitrate flask, and the distilled water was neutral. The amount of carbon dioxide produced in the reaction was ascertained by determining the excess of baryta with oxalic acid solution.\* The precipitate which had been formed in the baryta flasks during the experiment was examined and found to consist of carbonate; there was no sulphide or cyanide either in the precipitate or in the solution.

The examination of the reaction mixture itself consisted in the determination of (*a*) the iron reduced, (*b*) the amount of sulphate formed (where the iron salt originally used was chloride or thiocyanate). The extent of the reduction of the iron was estimated by titration with titanium trichloride, and the sulphate by precipitation with barium chloride, after removal of the iron.

Table II contains a summary of the results obtained from experiments conducted at the ordinary temperature, the quantities being stated in grams per litre of the reaction mixture.

TABLE II.

Iron salt.	Ferric iron originally present.	Iron reduced during the experi- ment.	$\text{H}_2\text{SO}_4$ stated as $\text{BaSO}_4$ .		Carbon dioxide.	
			Found.	Calc.	Found.	Calc.
Chloride .....	11.26	2.42	1.28	1.26	0.249	0.238
Sulphate .....	37.20	7.55	—	—	0.765	0.722
Sulphate .....	21.40	4.20	—	—	0.407	0.413
Thiocyanate .....	9.60	4.69	2.54	2.41	—	—
Thiocyanate .....	9.60	4.83	2.58	2.51	—	—

In the first three cases the reaction mixture contained initially 100 grams of potassium thiocyanate per litre. Further, in the first case, so much hydrochloric acid was added that the mixture was one-twentieth normal with respect to this acid. No acid was added in the case of the sulphate experiments, in the second of which air, free from carbon dioxide, was employed instead of nitrogen. The solutions of ferric thiocyanate were prepared by treating freshly precipitated and carefully washed ferric hydroxide with thiocyanic acid, insufficient to dissolve the whole. After some time the excess

\* Special experiments in which a known weight of sodium carbonate was added to an excess of dilute sulphuric acid showed that by the aspiration method carbon dioxide could be extracted almost quantitatively, the deficiency being not more than about 1 per cent.

of ferric hydroxide was removed by filtration, and the filtrate was taken as the reaction mixture. Even by this time considerable reduction had taken place, and since some of the carbon dioxide formed during the reduction might have escaped before the ferric thiocyanate solution was ready, the amount of sulphate only is recorded for the last two experiments in the foregoing table.

If it is assumed that corresponding with the reduction of the iron there is an oxidation of the thiocyanate, such that carbon is converted into carbon dioxide, and sulphur into sulphate, whilst nitrogen yields ammonia, it follows that for every eight gram-atoms of iron reduced, there should be formed 1 gram-molecule of carbon dioxide, 1 gram-molecule of sulphuric acid, and 1 gram-molecule of ammonia; that is, for every 4.48 grams of iron reduced there should be formed, on the foregoing assumption, 0.44 gram of carbon dioxide, 0.98 gram of sulphuric acid (= 2.33 grams barium sulphate), and 0.17 gram of ammonia. The figures for carbon dioxide and barium sulphate, calculated on this basis from the amount of iron reduced, are shown in the above table alongside the experimentally determined quantities of these substances; it will be seen that there is a very fair agreement between the observed and calculated figures. The ammonia produced in the reaction mixture was determined in one or two cases by adding excess of alkali and distilling into standard acid, but the amount so found was never more than about two-thirds of that calculated on the foregoing basis. It was thought that possibly the estimation of this compound\* by distillation from an alkaline liquid containing large quantities of potassium thiocyanate might be inaccurate, but special experiments carried out with the object of testing this point showed that ammonia could be recovered quantitatively from such a solution. It is therefore evident that only part of the nitrogen from the oxidised thiocyanate is converted into ammonia, and no definite information has been obtained as to the nature of the other product or products.

In addition to the sulphate and carbon dioxide, which are almost exclusively the products of oxidation at the ordinary temperature, mention should be made of other substances which were detected in very small quantity. These were: (1) hydrocyanic acid, (2) a yellow precipitate, which separated from the reaction mixture, and consisted probably of perthiocyanic acid or  $\psi$ -thiocyanogen (compare Chattaway and Stevens, T., 1897, **71**, 607; Stokes and Cain, *J. Amer. Chem. Soc.*, 1907, **29**, 413). The amount of hydrocyanic acid produced was extremely small, as was indicated by weighing the precipitate obtained in the flask containing silver nitrate; this precipitate was shown to contain no thiocyanate. In one experi

ment in which the amount of iron reduced was 4.2 grams per litre of the reaction mixture, the corresponding silver cyanide precipitate weighed only 0.021 gram.

Experiments similar to the above were carried out at higher temperatures, namely, at 39° and 60°. At the lower temperature air freed from carbon dioxide was aspirated through the apparatus; at the higher temperature, nitrogen freed from carbon dioxide was employed. The quantitative examination of the reaction mixture in all these cases was confined to a determination of (a) the amount of iron reduced, and (b) the amount of carbon dioxide formed. The results of these experiments are summarised in the following table, in which, as before, the figures indicate grams per litre of the reaction mixture.

TABLE III.

Temp.	Iron salt.	Iron reduced		Carbon dioxide.	
		Ferric iron originally present.	during the experiment.	Found.	Calc.
39	Sulphate	12.70	6.34	0.622	0.622
39	Chloride	10.89	3.37	0.324	0.331
60	Sulphate	16.27	12.82	1.280	1.260
60	Sulphate	42.70	16.77	1.615	1.645

In a similar experiment, carried out at 60° with chloride as the iron salt (10.80 grams of iron per litre of the reaction mixture), there was complete reduction in three days, but the amount of carbon dioxide found was 1.16 grams, as compared with 1.06 grams, calculated on the basis described above. In this case, however, there was a large deposit of yellow solid in the reaction flask, and a considerable black precipitate consisting of sulphide and cyanide in the silver nitrate flask, whilst sulphide was detected also in the contents of the first baryta flask. Probably this may be connected with the production of carbonyl sulphide, and its hydrolysis in the absorption flasks; an odour suggestive of this compound was detected on opening the reaction flask. In the sulphate experiments, on the other hand, which are recorded in Table III, the slight precipitate obtained in the silver nitrate flask had merely a grey tinge, and the contents of the first baryta flask were quite free from sulphide. Qualitative experiments at 80° indicated that in the case of both sulphate and chloride, the quantity of hydrocyanic acid produced is much larger than at 60°; further, the mixture of ferric chloride and thiocyanate gave a large, yellow deposit in a comparatively short time. At 100° the mixture of ferric salt and thiocyanate evolves hydrogen sulphide as well as hydrocyanic acid, although this is more marked with the chloride than with the sulphate.

It is worth noting that experiments carried out with ethereal solutions of ferric thiocyanate at the ordinary temperature showed no measurable reduction in two days, although in an aqueous solution, under the same conditions of temperature and concentration, about one-third of the ferric iron would have been reduced in this time.

*Velocity of the Reaction between Ferric Salts and Thiocyanates*

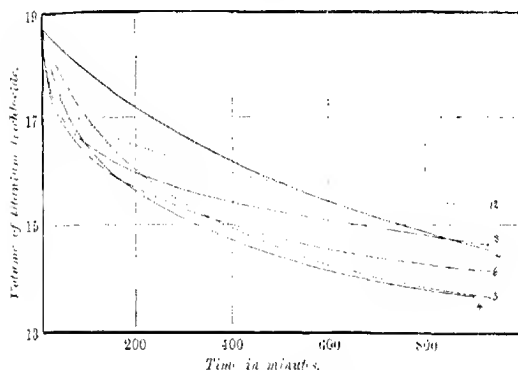
When the thiocyanate is present in a proportion smaller than corresponds with the composition of ferric thiocyanate,  $\text{Fe}(\text{CNS})_3$ , the velocity of reduction, at least in its initial stages, is very much lower than when the thiocyanate is in excess. The variation in the velocity with concentration is clearly shown by a series of experiments, carried out at  $25^\circ$ . In these, a constant quantity of ferric sulphate solution was mixed with different quantities of a strong solution of potassium thiocyanate, the mixture being made up to the same volume in each case. Hence the initial concentration of the iron was the same (8.67 grams of iron per litre) in each experiment of the series, whilst the concentration of the thiocyanate varied. The volume of a standard titanium trichloride solution required initially for 5 c.c. of each mixture was 18.70 c.c., and the following tables show the volumes of titanium trichloride required at intervals for 5 c.c. of the different mixtures.

TABLE IV.

Time in minutes.	Vol. $\text{TiCl}_3$ .	Time in minutes.	Vol. $\text{TiCl}_3$ .
1Fe : 2KCNs.		1Fe : 6KCNs.	
0	18.70	0	18.70
67	18.10	23	17.30
157	17.45	55	16.75
297	16.68	95	16.35
496	15.82	281	15.38
689	15.23	573	14.61
880	14.67	865	14.23
[120 hours	14.50]	[120 hours	13.35]
1Fe : 3KCNs.		1Fe : 8KCNs.	
0	18.70	0	18.70
21	18.00	18	17.59
64	17.40	50	16.95
213	15.90	138	16.39
300	15.00	372	15.50
599	14.32	660	15.00
877	13.74	857	14.75
[120 hours	12.90]	[120 hours	14.05]
1Fe : 4KCNs.		1Fe : 12KCNs.	
0	18.70	0	18.70
39	17.65	12	17.75
61	16.95	46	17.39
150	16.00	82	17.00
290	15.18	189	16.50
585	14.20	559	15.68
873	13.73	849	15.43
[120 hours	12.46]	[120 hours	14.90]

The results recorded in the foregoing table are represented graphically by the curves in Fig. 1, which are numbered according to the initial molecular proportion of potassium thiocyanate to one atom of iron. It will be seen that, although the very first portions of the curves which correspond with the ratios 1:6, 1:8, and 1:12 are practically indistinguishable, yet clearly the initial rate of reduction is much greater when the proportion of thiocyanate is high than when it is low; as time proceeds, however, the velocities in the former case fall off more rapidly than in the latter case. A striking illustration of this is furnished by the curves for the

FIG. 1.



proportions 1Fe:2KCN, and 1Fe:12KCN. The latter curve in its early course is very steep, but the slope soon falls off, and the curve is cut by the curve 2, the slope of which, although much less steep at the beginning, remains more uniform. A study of the figure will show that the other curves are of a character intermediate between these two extreme cases. Further, titrations of the mixtures made some days later (see figures in brackets in the foregoing table) showed clearly that the reaction had proceeded farthest in the mixture containing the smallest proportion of thiocyanate, and had made least progress in the case where the initial concentration of thiocyanate was greatest. It should be mentioned that similar experiments to those recorded in Table IV were made at 40°, and the character of the curves obtained exhibits a close resemblance to those shown in Fig. 1.

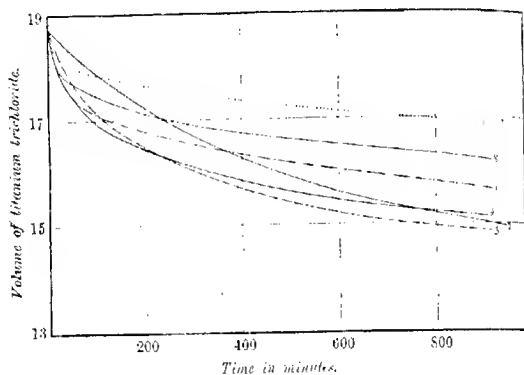
It is obvious that the influence of mass on the velocity of reduction of ferric salts by thiocyanates is not capable of any simple mathematical formulation, but the following experiments appear to



indicate that the acid produced in the reduction of the ferric salt is mainly responsible for the peculiar relationships expressed in Table IV and Fig. 1.

The initial addition of acid to mixtures of ferric sulphate and potassium thiocyanate produces an effect which depends on the relative proportions of the iron and the thiocyanate. When the thiocyanate is in very large excess, the presence of acid markedly retards the reaction, whilst with the ratio 1Fe:1.5KCNs the velocity, at least for the first third of the change, is the same whether acid has been added or not.

FIG. 2



The evidence bearing on the influence of acids is incorporated in Table V and Fig. 2. These experiments were in all respects parallel to those recorded in Table IV, except that all the solutions were now initially made 0.25*N* with respect to sulphuric acid. The concentrations of ferric sulphate and potassium thiocyanate were exactly the same as for the six mixtures already investigated, and the temperature was 25°.

TABLE V.

Time in minutes.	Vol. $\text{TiCl}_3$	Time in minutes.	Vol. $\text{TiCl}_3$
0	18.79	0	18.70
35	18.40	23	17.84
70	18.10	58	17.02
179	17.35	195	17.10
315	16.48	211	16.66
585	15.65	573	15.76
830	15.15	818	15.76
[28 hours	11.07]	[28 hours	15.35]

TABLE V. (continued).

Time in minutes.	Vol. $\text{TiCl}_3$	Time in minutes.	Vol. $\text{TiCl}_3$
$\text{1Fe: 3KCN} \left\{ \begin{array}{l} 0 \\ 31 \\ 66 \\ 113 \\ 251 \\ 586 \\ 826 \end{array} \right.$	$\left\{ \begin{array}{l} 18.70 \\ 18.96 \\ 17.50 \\ 17.01 \\ 16.27 \\ 15.27 \\ 14.95 \end{array} \right.$	$\text{1Fe: 2KCN} \left\{ \begin{array}{l} 0 \\ 19 \\ 54 \\ 101 \\ 330 \\ 596 \\ 818 \end{array} \right.$	$\left\{ \begin{array}{l} 18.70 \\ 17.97 \\ 17.79 \\ 17.45 \\ 16.85 \\ 16.55 \\ 16.30 \end{array} \right.$
[28 hours	14.25]	[28 hours	15.90]
$\text{1Fe: 4KCN} \left\{ \begin{array}{l} 0 \\ 27 \\ 62 \\ 108 \\ 247 \\ 412 \\ 822 \end{array} \right.$	$\left\{ \begin{array}{l} 18.70 \\ 17.76 \\ 17.30 \\ 16.85 \\ 16.27 \\ 15.89 \\ 15.20 \end{array} \right.$	$\text{1Fe: 2KCN} \left\{ \begin{array}{l} 0 \\ 15 \\ 50 \\ 97 \\ 230 \\ 425 \\ 810 \end{array} \right.$	$\left\{ \begin{array}{l} 18.70 \\ 18.24 \\ 18.03 \\ 17.87 \\ 17.69 \\ 17.30 \\ 16.98 \end{array} \right.$
[28 hours	14.58]	[28 hours	16.62]

The results recorded in the foregoing table are represented graphically in Fig. 2, which is on the same scale as Fig. 1. A comparison will show that whereas curve 2 is only slightly higher in Fig. 2 than in Fig. 1, curve 12 is displaced upwards to a very notable extent, whilst the displacement of the other curves is intermediate. The different influence of acid on the velocities for the 1:2 and 1:12 mixtures is well shown by the different positions of the points of intersection of the corresponding curves. It is interesting to note, also, that the extent of reduction in the 1:2 mixtures was, after twenty-eight hours, greater than in any of the other mixtures (see foregoing table).

It appears from these results that the peculiar relationship of the curves shown in Fig. 1 is probably connected with the presence of acid; this, as shown by the equation suggested on p. 796, is produced in the course of the reduction, and its amount obviously increases with time. Now experiments with solutions which contained initially the same amounts of ferric sulphate and potassium thiocyanate, but different quantities of sulphuric acid, have shown that the rate of reduction diminishes as the concentration of acid increases. The ratio  $\text{Fe:KCN}$  in these experiments was 1:4, and the temperature was  $25^\circ$ . The figures in the following table represent the volumes of titanium trichloride required for a given volume of four reaction mixtures, the first of which contained no added acid, whilst the others were initially made 0.25*N*, 0.50*N*, and 1.00*N* with respect to sulphuric acid.

TABLE VI.

Time in minutes.	No acid.	0.25 <i>N</i> $\text{H}_2\text{SO}_4$ .	0.50 <i>N</i> $\text{H}_2\text{SO}_4$ .	1.00 <i>N</i> $\text{H}_2\text{SO}_4$ .
0	63.5	63.5	63.5	63.5
50	61.5	62.3	62.3	63.1
100	60.6	61.6	62.3	62.8
200	59.6	60.8	61.7	62.3
VOL. $\text{CHCl}_3$ .				3 G

Another factor that bears on the peculiar character of the curves in Fig. 1 is the progressive diminution in the ratio of ferric iron to thiocyanate, which, on the basis of the equation on p. 796, is involved in the reaction. This circumstance, as well as the gradually increasing quantity of acid present, would tend to bring about a retardation of the reduction.

Experiments were also made on the influence of acids for solutions in which the initial ratio of ferric iron to thiocyanate was greater than 1:2. Ammonium thiocyanate was employed in these experiments, the initial ratio Fe:  $\text{NH}_4\text{CNS}$  being 1:0.9 in each case. The effects of different quantities of sulphuric acid are shown in Table VII, the figures in which, like those in Table VI, represent the volumes of titanium trichloride solution required for a given volume of the reaction mixture. The temperature was 60°.

TABLE VII.

Time in minutes.	No acid.	0.1N- $\text{H}_2\text{SO}_4$ .	0.2N- $\text{H}_2\text{SO}_4$ .	0.4N- $\text{H}_2\text{SO}_4$ .
0	49.0	49.0	49.0	49.0
20	42.7	42.1	40.7	39.6
50	37.6	36.6	35.0	33.5
100	32.7	31.6	30.0	28.6

It will be seen that the greater the initial concentration of acid the greater is the velocity of reduction. Similar experiments, carried out at 40° with two solutions of ferric sulphate and potassium thiocyanate (ratio 1Fe:1KCNs), one of which contained no added acid, and the other was initially 0.25N with respect to sulphuric acid, confirmed the view that for this ratio of ferric iron to thiocyanate, acid definitely accelerates the reduction.

An attempt was made to secure evidence bearing on the order of the reaction between ferric salts and thiocyanates by experiments in which the thiocyanate was in very large excess, whilst the concentration of the iron salt varied. In these experiments, three of which, carried out at 40°, are recorded below in Table VIII, the

TABLE VIII.

Fractional reduction of the iron.	Times in minutes.		
	a.	b.	c.
0.05	1.5	1.7	2.0
0.10	4.0	4.0	4.0
0.15	7.7	7.8	7.7
0.20	13.5	14.6	14.0
0.25	23.3	25.6	26.7
0.30	42.6	47.5	49.0
0.35	75.0	82.5	89.0
0.40	122.0	137.5	158.0

initial concentration of ammonium thiocyanate was in each case 75 grams per litre; in (a) the ratio of iron to thiocyanate,  $\text{Fe}:\text{NH}_4\text{CNS}$ , was 1:18, in (b), 1:13.5, and in (c), 1:9. The curves representing the rate of reduction were deduced as usual, and from these the times (in minutes) necessary for a given fractional reduction of the iron were read off. These times are recorded in Table VIII.

From the figures in the table it is apparent that, where the thiocyanate is in large excess and for the first quarter of the reaction, the time necessary for the reduction of a given fraction of the iron is almost independent of the initial concentration of the iron. The conclusion may be drawn therefore that in its early stages the reaction is unimolecular with respect to the iron. After the first portion of the change is over, the foregoing simple relationship holds no longer, the time necessary for the completion of a given fractional reduction being then least for (a), and greatest for (c). In view of the effect of acids on the rate of reduction, it is not surprising that the course of the reaction cannot be formulated on the usual lines. Further experiments are being made with the object of gaining further information as to the mechanism of the change.

The influence of temperature on the velocity of interaction of ferric salts and thiocyanates is very marked. It is not possible to state the value of the temperature-coefficient, but an idea of the relative velocities at different temperatures may be gained from the following observations. Experiments made with a given mixture of ferric sulphate and potassium thiocyanate (ratio  $\text{Fe}:\text{2KCNS}$ ) at two temperatures,  $25^\circ$  and  $40^\circ$ , showed that the times necessary for the reduction of one-fifth of the iron were respectively 760 and 94 minutes.

It was thought that the velocity of the reaction between ferric salts and thiocyanates might be affected by light. Experiments were therefore made in which equal portions of a given mixture of ferric sulphate and potassium thiocyanate were placed in narrow test-tubes, and either kept in the dark or exposed to diffuse daylight. It was found after four weeks that the extent of reduction in the exposed tubes was exactly the same as in those which had been kept in the dark. It was observed, however, that the slight yellow deposit obtained in all the solutions formed preferentially, in the case of those exposed to light, on the wall of the tube next the light.

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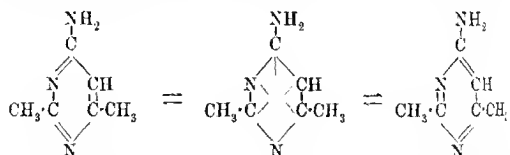
LXXXIII.—*Non-aromatic Diazonium Salts. Part 1.*  
*Antipyrinediazonium Salts and their Azo-derivatives.*

By GILBERT T. MORGAN and JOSEPH REILLY, B.A., B.Sc., A.R.C.Sc.I

THE greatest development in the chemistry of diazo-compounds has taken place in connexion with aromatic amines, owing mainly to two facts: the important technical employment of benzenoid and naphthalenoid diazo-derivatives in the manufacture of azo-dyes, and the manifold applications of the diazo-reaction to synthetic operations in the aromatic series.

It is, however, known that certain non-aromatic amines possess in varying degrees the property of diazotisability, and the object of the present investigation is to ascertain within what limits this reaction is manifested by bases which do not contain amino-groups attached to aromatic nuclei. The property of diazotisability appears to be connected with the presence in the basic molecule of an unsaturated group, for hitherto it has not been found possible to diazotise the salt of any primary base having its amino-group attached either to a fully saturated radicle or to a completely hydrogenised ring. These two cases may be exemplified respectively by the aliphatic primary amines and by bornylamine and *ac*-tetrahydro-*β*-naphthylamine. On the other hand, there are many bases with amino-groups attached to unsaturated complexes which are not diazotisable.

For example, the authors have not succeeded in diazotising 6-amino-2:4-dimethylpyrimidine (cyanmethine), a base possessing a six-membered cyclic ring closely akin to that of the benzene nucleus, with the same possibility of ethenoid and centric arrangements of the valencies:



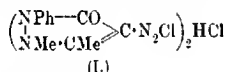
In spite of the close analogy to aniline and its homologues, this base behaves as an aliphatic amine, and yields the corresponding 6-hydroxy-2:4-dimethylpyrimidine on treatment with nitrous acid\*. The orientation of the amino-group in the foregoing base with

\* It has recently been noticed (this vol., p. 72) that 2-amino-1:4-naphthoquinonemide is not diazotisable, although the basic group is attached to an unsaturated complex derived from dihydronaphthalene.

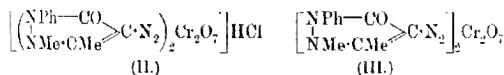
regard to cyclic nitrogen is, in all probability, not without importance, for Mills and Watson have shown that 3-aminoquinoline is readily diazotisable, differing in that respect from 2- and 4-aminoquinolines, which have not yielded diazonium salts (T., 1910, 97, 741).

The researches of Knorr and his collaborators have demonstrated that certain bases of the pyrazole series are diazotisable, giving rise to very stable diazo-derivatives, which, however, have hitherto only been obtained in solution. These diazo-compounds, like the aromatic diazonium salts, couple with alkaline  $\beta$ -naphthol, and furnish diazoamines with aniline, but with the exception of the preparation of triazoantipyrene by Forster and Müller (T., 1909, 95, 2072), they have not been employed successfully in syntheses involving the replacement of the diazo-group by other radicles.

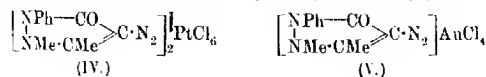
As a preliminary step in the closer study of the diazo-derivatives of the pyrazole series, the authors have isolated 1-phenyl-2:3-dimethylpyrazolone-4-diazonium chloride, produced by diazotising 4-amino-1-phenyl-2:3-dimethylpyrazolone (4-aminoantipyrene). The hydrochloride of this base, when treated with ethyl nitrite in alcoholic solution, yields, on concentration, a syrupy residue, but when diazotisation is effected in the presence of excess of hydrochloric acid, a crystalline, hygroscopic salt is obtained having the following constitution:



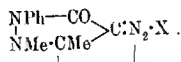
The additional molecule of hydrogen chloride is probably attracted to the complex by the basic nitrogen atoms of the pyrazolone rings, but it should be mentioned that acid diazonium salts have been observed in the aromatic series, although in such cases their stability has been less than that of the normal salts Hirsch, *Ber.*, 1897, 30, 1148; Hantzsch, *ibid.*, 1153). From the foregoing acid chloride the corresponding *dichromate hydrochloride* was obtained, which, when dried under diminished pressure, over potassium hydroxide, slowly lost its volatile acid, and became converted into the normal *dichromate*:



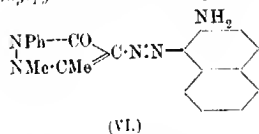
The *platinichloride* and *aureichloride* containing the normal amounts of acidic constituents have also been obtained.



The existence of these normally constituted diazonium salts containing the pyrazolone ring is of some interest in connexion with current theories of the structure of diazo-compounds, inasmuch as it justifies the contention that co-ordination between the diazonium complex and the unsaturated ring may involve a contiguous carbon atom as well as one in the para-position (T., 1907, **91**, 1315; 1908, **93**, 617). The para-hemiquinonoid formula advocated by Cain is inapplicable to these pyrazolonediazonium salts (compare Forster and Müller, *loc. cit.*). Representing this co-ordination as being due to a rearrangement in the principal valencies, then the general formula for these diazonium salts would be:



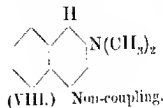
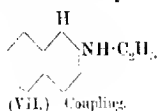
1-Phenyl-2:3-dimethylpyrazolone-4-diazonium chloride couples readily with the more reactive aromatic bases yielding azo-derivatives. With *m*-phenylenediamine, it furnishes an azo-colour of the chrysoidine group, and with  $\beta$ -naphthylamine it gives rise to 1-phenyl-2:3-dimethylpyrazolone-4-azo- $\beta$ -naphthylamine:



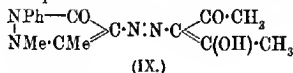
an aminoazo-derivative distinguished from the arylazo- $\beta$ -naphthylamines by its power of forming intense bluish-purple salts with mineral or organic acids, which are so stable in aqueous solution that the azo-base can be used as an indicator in acidimetry and alkalimetry. This property, like that of forming the foregoing acid diazonium chloride, is to be correlated with the basic nature of the pyrazolone ring.

An interesting parallelism was noticed in the coupling of the antipyrinediazonium salts with  $\beta$ -naphthylamine and its derivatives on the one hand, and the  $\beta$ -diketones and  $\beta$ -keto-esters on the other. In both cases the condensation takes place only when two mobile hydrogen atoms are present.

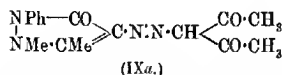
An azo-derivative is readily produced from ethyl- $\beta$ -naphthylamine (VII), but no reaction takes place with dimethyl- $\beta$ -naphthylamine (VIII), which has only the one reactive hydrogen atom:



Acetylacetone and the antipyrinediazonium salts readily couple, yielding an azo-compound:

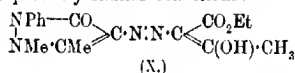


or

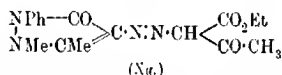


The azo-constitution for this substance, 1-phenyl-2:3-dimethylpyrazolone-4-azoacetylacetone, is justified by the fact that it yields, even in aqueous solution, a sparingly soluble alkali derivative, which develops the enolic red coloration with ferric chloride and furnishes an olive-green copper derivative. These reactions render very improbable a hydrazone configuration, and support the enolic formula (IX) for the sodium derivative; they do not, however, serve to exclude the ketonic constitution (IXa) for the free azo-compound.

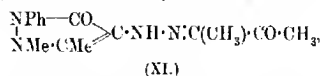
Ethyl 1-phenyl-2:3-dimethylpyrazolone-4-azoacetoacetate (X or Xa) closely resembles the foregoing azo-acetylacetone, and is obtained under precisely similar conditions:



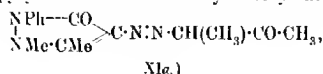
or



With methyl acetyethyl ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}\cdot\text{CH}_3$ , which, like dimethyl- $\beta$ -naphthylamine, contains only one labile hydrogen (\*), the reaction takes a different course. Coupling occurs, but it is accompanied by hydrolysis, involving the elimination of an acetyl group, so that the parent ketone is ethyl methyl ketone. The pale yellow product differs from the antipyrilazoacetylacetone in not giving an alkali derivative with aqueous sodium hydroxide. This difference may be explained by regarding the compound as an antipyrillhydrazone of dimethyl diketone:



or as an antipyrilazo-derivative of ethyl methyl ketone:





which is no longer capable of assuming the enolic form, and therefore does not yield metallic derivatives.

The study of these condensation products from antipyrine diazonium salts and the  $\beta$ -diketo-compounds is being continued.

#### EXPERIMENTAL.

##### *1-Phenyl-2:3-dimethylpyrazolone-4-diazonium Chloride* (Formula I).

4-Aminoantipyrine hydrochloride (m. p.  $232^{\circ}$ ), obtained by successively reducing 4-nitrosoantipyrine, extracting the crude base in the form of its benzylidene derivative, hydrolysing the latter with dilute hydrochloric acid, and removing the benzaldehyde with ether, was purified by repeated crystallisation from alcohol, and used in the following experiments.

(1) The diazo-solution, produced by treating the purified salt with ethyl nitrite in absolute alcohol, left on evaporation a syrupy residue, which after two months had lost its power of coupling with alkaline  $\beta$ -naphthol.

(2) The salt dissolved in alcohol containing hydrochloric acid (3 mols.) was treated with ethyl nitrite in slight excess. The solution was concentrated in a vacuum desiccator over potassium hydroxide until the acid diazonium chloride separated in stellate aggregates of almost colourless, hygroscopic crystals, which retained their coupling power with  $\beta$ -naphthol after three months:

0.1468 gave 0.2596  $\text{CO}_2$  and 0.0485  $\text{H}_2\text{O}$ . C = 48.23; H = 3.68.

0.1215 „ 21.6  $\text{N}_2$  at  $17^{\circ}$  and 752 mm.\* N = 20.63.

0.1605 „ 0.1272 AgCl. Cl = 19.61.

0.1422 „ 0.1115 AgCl. Cl = 19.39.

$(\text{C}_{11}\text{H}_{11}\text{ON}_3\text{Cl})_2 \cdot \text{HCl}$  requires C = 49.12; H = 4.28; N = 20.85;  
Cl = 19.79 per cent.

The chlorine determinations were made on different preparations, one of which had been heated on the water-bath in alcoholic solution in order to remove excess of ethyl nitrite. The diazonium chloride was insoluble in dry ether.

Reduction of this diazonium salt with stannous chloride does not lead to the formation of a readily isolated hydrazine, owing probably to condensation taking place between the newly formed hydrazine group and the carbonyl radicle present in the pyrazolone ring.

The diazonium chloride and the corresponding nitrate were both very stable in hot aqueous solutions, but the coupling power, which persisted under these conditions, disappeared entirely when the chloride was digested with moist silver oxide, the filtrate from silver

\* In this and the following nitrogen estimations the gas was measured over 50 per cent. potassium hydroxide solution.

chloride giving no azo-colour. When treated successively with sodium hydroxide (3 mols.) and cold dilute acetic acid, the diazonium salt lost completely its coupling power. Potassium cyanide added to an acid solution of the diazonium salt had the same destructive effect; a white, unstable diazo-cyanide was precipitated, which rapidly became yellow, and then black. Potassium thiocyanate produced a white precipitate with the diazonium chloride, which darkened on exposure to air.

*1-Phenyl-2:3-dimethylpyrazolone-4-diazonium Dichromate Hydrochloride (Formula II).*

The salt separated in orange-yellow, acicular crystals on adding aqueous chromium trioxide to a solution of the acid diazonium chloride:

0.1922 gave 0.0428 AgCl and 0.0425  $\text{Cr}_2\text{O}_3$ .  $\text{Cl}=5.51$ ;  $\text{Cr}=15.13$ .  
 $\text{C}_{22}\text{H}_{22}\text{O}_9\text{N}_8\text{ClCr}_2$  requires  $\text{Cl}=5.20$ ;  $\text{Cr}=15.24$  per cent.

When dried for several weeks in a vacuum desiccator over solid potassium hydroxide, hydrogen chloride was slowly eliminated, and although the salt still contained some chlorine ( $\text{Cl}=1.93$  per cent.), its composition now corresponded closely with that of 1-phenyl-2:3-dimethylpyrazolone-4-diazonium dichromate (III):

0.1940 gave 0.0460  $\text{Cr}_2\text{O}_3$ .  $\text{Cr}=16.22$ .  
 0.2868 " 0.0673  $\text{Cr}_2\text{O}_3$ .  $\text{Cr}=16.03$ .  
 0.1620 " 24.5 c.c.  $\text{N}_2$  at  $21.5^\circ$  and 765 mm.  $\text{N}=17.54$ .  
 0.0976 " 14.6 c.c.  $\text{N}_2$  "  $21^\circ$  " 765 mm.  $\text{N}=17.38$ .  
 $\text{C}_{22}\text{H}_{22}\text{O}_9\text{N}_8\text{Cr}_2$  requires  $\text{Cr}=16.10$ ;  $\text{N}=17.34$  per cent.

The dichromate, although stable at the ordinary temperature, exploded on heating or by percussion. When heated to  $120^\circ$  in a strong aqueous solution of sulphuric acid, only about half the diazo-nitrogen was eliminated.

*1-Phenyl-2:3-dimethylpyrazolone-4-diazonium Platinichloride (Formula IV).*

On mixing aqueous solutions of chloroplatinic acid and the foregoing diazonium chloride, an almost quantitative precipitation occurred of the crystalline, yellow diazonium platinichloride. This salt, after drying in the desiccator, remained constant in weight up to  $120^\circ$ :

0.1618 gave 0.1920  $\text{CO}_2$  and 0.0455  $\text{H}_2\text{O}$ .  $\text{C}=31.77$ ;  $\text{H}=3.07$ .  
 0.2477 " 29.8 c.c.  $\text{N}_2$  at  $20^\circ$  and 751 mm.  $\text{N}=13.75$ .  
 0.1492 " 17.8 c.c.  $\text{N}_2$  "  $20^\circ$  " 746 mm.  $\text{N}=13.55$ .  
 0.2278 " 0.233 AgCl.  $\text{Cl}=25.30$ .  
 0.1161 " 0.0271 Pt.  $\text{Pt}=23.34$ .  
 $\text{C}_{22}\text{H}_{22}\text{O}_9\text{N}_8\text{Cl}_6\text{Pt}$  requires  $\text{C}=31.50$ ;  $\text{H}=2.63$ ;  $\text{N}=13.37$ ;  
 $\text{Cl}=25.38$ ;  $\text{Pt}=23.29$  per cent.

1-Phenyl-2:3-dimethylpyrazolone-4-diazonium Aurichloride  
(Formula V).

This salt was obtained as a golden-yellow, crystalline precipitate on mixing aqueous solutions of the diazonium chloride and chloroauric acid:

0.1520 gave 0.1330  $\text{CO}_2$  and 0.0323  $\text{H}_2\text{O}$ .  $\text{C} = 23.86$ ;  $\text{H} = 2.36$ .

0.1893 „ 16.6 c.c.  $\text{N}_2$  at  $17^\circ$  and 758 mm.  $\text{N} = 10.25$ .

0.1476 „ 0.1535  $\text{AgCl}$ .  $\text{Cl} = 25.72$ .

0.1890 „ 0.0672  $\text{Au}$ .  $\text{Au} = 35.55$ .

$\text{C}_{11}\text{H}_{11}\text{ON}_4\text{Cl}_4\text{Au}$  requires  $\text{C} = 23.83$ ;  $\text{H} = 1.99$ ;  $\text{N} = 10.11$ ;  
 $\text{Cl} = 25.60$ ;  $\text{Au} = 35.59$  per cent.

The three foregoing diazonium salts are all very stable compounds, coupling with alkaline  $\beta$ -naphthol after several months to form a red azo-compound. In the case of the aurichloride the red colour soon changes to brown unless the gold is previously removed as sulphide, when the red coloration persists.

1-Phenyl-2:3-dimethylpyrazolone-4-azo- $\beta$ -naphthylamine  
(Formula VI).

On adding a solution in dilute hydrochloric acid of the diazonium chloride to alcoholic  $\beta$ -naphthylamine, a deep blue coloration was immediately developed, and the solution rapidly became almost solid, owing to the separation of the sparingly soluble, dark blue hydrochloride of the aminoazo-derivative. From this salt the aminoazo-base was set free by ammonia and crystallised repeatedly from alcohol, in which it was somewhat sparingly soluble. The base separated in orange-red biaxial needles, darkening at  $234^\circ$ , and melting at  $235^\circ$ :

0.0635 gave 10.9 c.c.  $\text{N}_2$  at  $20^\circ$  and 755 mm.  $\text{N} = 19.73$ .

$\text{C}_{21}\text{H}_{19}\text{ON}_3$  requires  $\text{N} = 19.61$  per cent.

This azo-base was sparingly soluble in the ordinary volatile organic media, more soluble in pyridine, but insoluble in water.

The hydrochloride was prepared by dissolving the base in glacial acetic acid, and adding hydrochloric acid; it crystallised in tufts of small, acicular, bluish-black crystals, with bronzy reflex, and decomposed at  $185^\circ$ :

0.1365 gave 20.5 c.c.  $\text{N}_2$  at  $17^\circ$  and 765 mm.  $\text{N} = 17.72$ .

0.2639 „ 0.0970  $\text{AgCl}$  and 0.2381 base.  $\text{Cl} = 9.12$ ; Base = 90.53.

$\text{C}_{21}\text{H}_{19}\text{ON}_3\text{HCl}$  requires  $\text{N} = 17.79$ ;  $\text{Cl} = 9.01$ ; Base = 90.73 per cent.

This salt was sparingly soluble in water and the ordinary organic media, but dissolved more readily in pyridine.

Comparative experiments were made with ethyl  $\beta$ -naphthylamine

and dimethyl- $\beta$ -naphthylamine. The former of these bases coupled with 1-phenyl-2:3-dimethylpyrazolonediazonium chloride in alcoholic solution, giving rise to an orange azo-derivative, which separated from alcoholic hydrochloric acid in the form of its dark, bronzy-blue hydrochloride.

Dimethyl- $\beta$ -naphthylamine did not couple with the diazonium salt under the foregoing experimental conditions, and the greater portion of the base was recovered unchanged.

$\beta$ -Naphthylamine-6-sulphonic acid (Brönnner acid), when dissolved in aqueous sodium carbonate and reprecipitated by acetic acid, coupled readily with the diazonium hydrochloride, yielding a dark blue azo-derivative (hydrochloride), which is decomposed by aqueous sodium acetate, giving rise to the reddish-orange azo-sulphonic acid.

The three foregoing azo-derivatives dissolved in concentrated sulphuric acid to deep red solutions, which assumed an intensely purple shade on dilution with water.

1-Phenyl-2:3-dimethylpyrazoloneazo- $\beta$ -naphthol, unlike the purely aromatic azo- $\beta$ -naphthols, assumes a dark reddish-purple tint on treatment with concentrated aqueous acids, its original colour, orange-red, being restored by alkalis.

#### *Condensation Products with the $\beta$ -Diketones.*

##### *1-Phenyl-2:3-dimethylpyrazolone-4-azoacetylacetone* (Formula IX or IXa).

4-Aminoantipyrine hydrochloride (1 mol.) was diazotised in cold dilute hydrochloric acid, the excess of nitrous acid removed by carbamide, and the solution added to acetylacetone (1 mol.) dissolved in alcohol. The addition of sodium acetate produced a yellow precipitate, which, when crystallised repeatedly from alcohol, separated in radiating masses of reddish-orange scales and biaxial, prismatic needles, melting at 181—182°:

0.1318 gave 0.2955  $\text{CO}_2$  and 0.0656  $\text{H}_2\text{O}$ . C = 61.15; H = 5.53.

0.1700 „ 26.6 c.c.  $\text{N}_2$  at 20° and 752 mm. N = 17.93.

$\text{C}_{14}\text{H}_{11}\text{O}_5\text{N}_4$  requires C = 61.15; H = 5.73; N = 17.83 per cent.

This azo compound was practically insoluble in water, sparingly soluble in ether, but dissolving more freely in other organic media, especially in chloroform.

Benzoylacetone, when coupled with the diazonium salt, gave a similar yellow azo-derivative.

1-Phenyl-2:3-dimethylpyrazolone-4-azoacetylacetone yielded a sparingly soluble, dark orange sodium derivative when treated with an excess (2 mols.) of concentrated aqueous sodium hydroxide. With ferric chloride the dilute aqueous solution of the sodium derivative

developed an intense red coloration, and with copper sulphate an olive-green copper derivative was precipitated.

*Ethyl 1-Phenyl-2:3-dimethylpyrazolone-4-azoacetate*  
(Formula X or Xa).

The antipyrinediazonium solution (1 mol.), prepared as in the preceding experiment, was added to an alcoholic solution of ethyl acetoacetate (1 mol.), followed by excess of sodium acetate. The product, a bulky, yellow precipitate, was crystallised repeatedly from alcohol, when it separated in fibrous masses of yellow, prismatic needles, melting at 174—175°:

0.1226 gave 0.2680 CO<sub>2</sub> and 0.0663 H<sub>2</sub>O. C=59.62; H=6.01.

0.1826 „, 25.5 c.c. N<sub>2</sub> at 15.5° and 748 mm. N=16.21.

C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>N<sub>4</sub> requires C=59.30; H=5.81; N=16.28 per cent.

The azo-compound was sparingly soluble in water, ether, or ethyl acetate; it dissolved more readily in other organic media, and especially in chloroform.

*Condensation Product of 1-Phenyl-2:3-dimethylpyrazolone-4-diazonium Chloride and Methyl Acetyl methyl Ketone*  
(Formula XI or XIa).

The antipyrinediazonium chloride solution, freed from excess of nitrous acid, was added to alcoholic methyl acetyl methyl ketone (1 mol.). On adding aqueous sodium acetate, a pale yellow precipitate was slowly formed, which, when crystallised repeatedly from alcohol, separated in lustrous, pale yellow, six-sided biaxial plates, melting at 199—200°:

0.2006 gave 0.4635 CO<sub>2</sub> and 0.1175 H<sub>2</sub>O. C=63.02; H=6.51.

0.1706 „, 23.9 c.c. N<sub>2</sub> at 18° and 756 mm. N=19.67.

C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>N<sub>4</sub> requires C=62.94; H=6.29; N=19.58 per cent.

The compound is less soluble than the preceding substances in the ordinary organic media, but it dissolved freely in chloroform or pyridine. With aqueous sodium hydroxide it gave no sodium derivative.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,  
DUBLIN.

LXXXIV.—*The Constitution of the Anhydro-bases derived from Tetrahydroberberine Alkyl Hydroxides.*

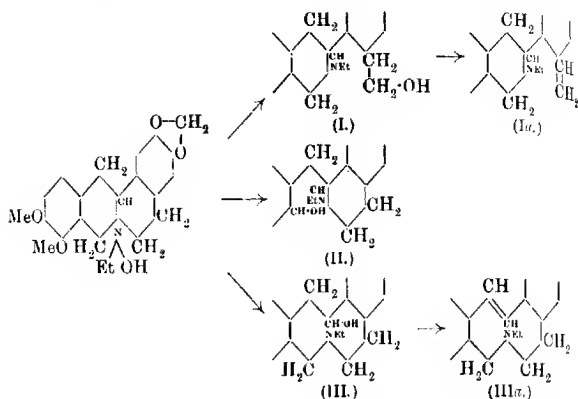
By FRANK LEE PYMAN.

The degradation of tetrahydroberberine by Hofmann's method, that is, the removal of the elements of water from tetrahydroberberine alkyl hydroxides has been the subject of several previous investigations.

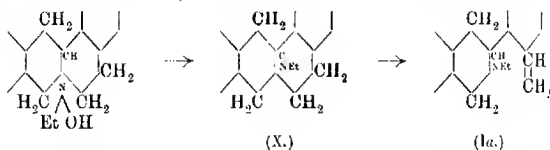
The point was first studied by E. Schmidt and his pupils, Court, Schreiber, Gaze, and Link (*Arch. Pharm.*, 1890, **228**, 596, 604; 1892, **230**, 287, 291; and *Dissertations*), the effect of heating the metho- and etho-hydroxides of tetrahydroberberine being examined. The resulting compounds, however, did not agree in their properties with those to be expected from true anhydro-bases, as E. Schmidt himself (*Arch. Pharm.*, 1892, **230**, 289) points out, since tetrahydroberberine alkyl iodides were regenerated from them by the action of alkyl iodides, whereas unsaturated alkyl iodide additive products should have been obtained.

Voss and Gadamer (*Arch. Pharm.*, 1910, **248**, 43), who next studied this subject, offered further evidence that the products obtained by the previous investigators were not the true anhydro-bases. These authors were the first to isolate a true anhydro-base derived from tetrahydroberberine. They dried tetrahydroberberine ethocarbonate in a vacuum on the water-bath to constant weight, and isolated from the product the ethyl anhydro-base, which melted at 132.5°. They also obtained the same base by evaporating *l*-canadine (*l*-tetrahydroberberine) ethohydroxide to dryness in a vacuum and working up the product so obtained; in this case, however, the presence of another product was observed, for the crude ether-soluble product (which would contain only tertiary bases, such as anhydro- and possibly carbinol bases) proved to be optically active, but the identity of this by-product was left to be cleared up later. The fact that the ethyl anhydro-base, melting at 132.5° was obtained from *l*-canadine as well as from tetrahydroberberine enabled Voss and Gadamer to deduce its constitution as follows.

Tetrahydroberberine ethohydroxide is capable of yielding three hypothetical carbinol bases, I, II, III, of which two, I and III, can lose water with formation of the corresponding anhydro-bases, Ia and IIIa respectively.

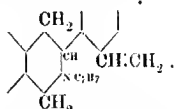


If the reaction proceeds according to the first scheme, the asymmetry of the asymmetric carbon atom is preserved, whereas according to the third scheme it is lost. Since therefore *l*-canadine ethohydroxide gave an optically inactive anhydro-base, the latter is to be formulated as IIIa. This conclusion has since been criticised by McDavid, Perkin, and Robinson (T., 1912, 101, 1218), who regarded this formula as improbable, since it contains a ten-membered ring, and in order to account for the production by Voss and Gadamer of an optically inactive anhydro-base from optically active *l*-canadine ethohydroxide by heat, suggested that the reactions involved were probably correctly represented in the scheme shown below, which was not further elaborated:



According to this view the reaction does not proceed through the hypothetical carbinol base, but the hydroxyl group attached to the nitrogen atom, together with a hydrogen atom from the asymmetric carbon atom, are together eliminated in the form of water, yielding the anhydro-base X, which then rearranges itself to the anhydro-base Ia. It may be pointed out that this method of representing the formation of an anhydro-base from its parent quaternary alkyl hydroxide is unusual, and is frankly designed to meet the particular case.

McDavid, Perkin and Robinson themselves actually studied experimentally the degradation of tetrahydroberberine benzyl chloride down to the nitrogen-free compound berberilene. The first step in this series was the conversion of the former compound into the corresponding anhydro-base, which was carried out by boiling with alcoholic potassium hydroxide. To the product, which was isolated in the form of its hydrochloride, they ascribed the constitution of *N*-benzylisotetrahydroberberine:



The views of Voss and Gadamer on the one hand, and of McDavid, Perkin, and Robinson on the other as to the constitution of their respective anhydro-bases are therefore divergent.

Quite recently, the present author, in collaboration with Jowett (this vol., p. 290), isolated *l*-canadine methochloride from *Contharophum Brachyacanthum*. Before the identity of this compound was established a quantity was converted into the corresponding anhydro-base, and evidence was obtained that this was not a simple substance, but a mixture, since its optical activity gradually diminished on repeated crystallisations.

Now Voss and Gadamer had found, as has already been noted, that the crude product obtained by the action of heat on *l*-canadine ethohydroxide was optically active, whilst, after purification, an optically inactive anhydro-base identical with that obtained from tetrahydroberberine ethohydroxide was obtained, and had reserved the further study of this point for a later occasion. As it seemed probable that the study of the effect of heat on the methohydroxide of *l*-canadine would yield valuable information as to the nature of the anhydro-bases produced, Prof. Gadamer was communicated with, and he very kindly expressed his willingness that the present author should continue the work.

The investigation has shown that when *l*-canadine methohydroxide evaporated to dryness in a vacuum, a mixture of no less than three isomeric anhydro-bases having the composition  $C_{21}H_{23}O_4N$  results. The melting points, optical behaviour, and yields in percentages of the theoretical are as follows:

	M. p.		Yield, per cent.
Base A.....	135—136° (corr.)	optically inactive	53
„ B.....	114—115 „	„	4
„ C.....	101—102 „	[α] <sub>D</sub> - 113.6°	12

The three bases behave as unsaturated compounds towards



bromine and permanganate, and each forms a characteristic hydrochloride and methiodide.

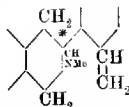
When the corresponding racemic compound, tetrahydroberberine methohydroxide, is similarly treated, the base *A* is obtained in 54 per cent. yield, and the base *B* in 19 per cent. yield. The yield of base *B* in this case is thus approximately equivalent to that of *B* + *C* in the case of *l*-canadine methohydroxide, and this suggests that *B* is the racemic form of *C*.

When, however, *l*-canadine methohydroxide is evaporated to dryness on the water-bath under atmospheric pressure, the base *A* is not found amongst the products of the reactions, but a mixture of *B* and *C* results.

Similarly, when tetrahydroberberine methohydroxide is evaporated to dryness on the water-bath, under atmospheric pressure, the base *A* is not found, and the only anhydro-base obtained is *B*. The yields in the two latter cases are only moderate owing to the neutralisation of a part of the methohydroxide by the carbonic acid of the atmosphere, for the carbonate so formed is not converted into anhydro-base by heating with water on the water-bath. This has been shown definitely by a separate experiment in which a quantity of tetrahydroberberine methohydroxide was saturated with carbonic acid and evaporated on the water-bath; as the evaporation proceeded, crystals of the carbonate separated, and even after concentration to a paste the product was completely soluble in hot water excepting a slight turbidity, and deposited crystals of the carbonate on cooling. The solutions of the carbonates resulting after the removal of the anhydro-bases *B* + *C* or *C* in the experiments described above can be caused to yield further quantities of these bases by the addition of alkali hydroxides which remove the carbonic acid. By this means, a yield of 71 per cent. of *B* and 11 per cent. of *C* has been obtained in the dehydration of *l*-canadine methohydroxide under atmospheric pressure, and a yield of 79 per cent. of *B* from tetrahydroberberine methohydroxide in similar circumstances.

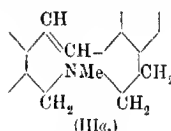
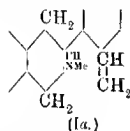
The preparation of the three bases having been described, it now remains to describe their properties and discuss their constitutions.

In the first place, the optically active base *C* can only have the constitution given below:



\* An asterisk over the asymmetric carbon atom denotes that the compounds are optically active.

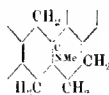
Now, a marked difference in behaviour is shown by the base *A* on the one hand, and the bases *B* and *C* on the other. In the first place, the hydrochloride of *A* is readily soluble in boiling water containing a little hydrochloric acid, whilst those of *B* and *C* are very sparingly soluble; secondly, whilst freshly prepared cold aqueous alcoholic solutions of the three bases are only faintly alkaline in their reaction to litmus, after short heating in the water-bath, the solution of *A* becomes very strongly alkaline, whilst the solutions of *B* and *C* are unchanged. Further, as has already been pointed out, when the optically inactive tetrahydroberberine methohydroxide is employed for the preparation of the anhydro-bases in the place of *l*-canadine methohydroxide, an additional quantity of *B* is found in the place of *C*. It follows that *B* is the racemic form of *C*, since there are only two\* optically inactive anhydro-bases, namely, *Ia* and *IIIa*, theoretically derivable from tetrahydroberberine methohydroxide, and of these *Ia* is the racemic form corresponding with the optically active base *C*. There can be no doubt,



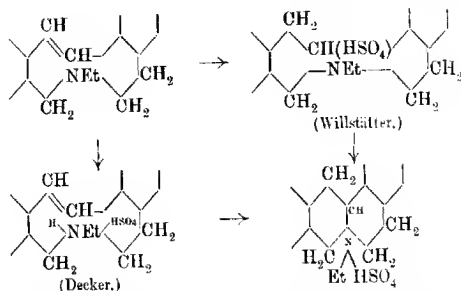
therefore, that *B* has the formula *Ia*, whilst *A* must then have the formula *IIIa*.

The behaviour of *A* with hot aqueous alcohol is entirely similar to that of Voss and Gadamer's anhydroethylcanadine, which, the latter authors showed, became converted into tetrahydroberberine methohydroxide in similar circumstances. They also showed that the salts of their base underwent a similar change, and represented it according to the schemes shown on p. 822, which depend on the adoption of Willstätter's (*Lundten*, 1903, 326, 4) and Decker's (*Ber.*, 1904, 37, 520) methods of representing such a change respectively:

\* The possibility that one of the anhydro-bases might have a formula analogous to McDavid, Perkin, and Robinson's intermediate product X (p. 818):



eliminated by the fact that each of the anhydro-bases forms a distinct unsaturated hydrochloride from which it can be prepared by treatment with ammonia, whereas a base of the above formula could only yield with hydrochloric acid the saturated pentenary salt, tetrahydroberberine methochloride.

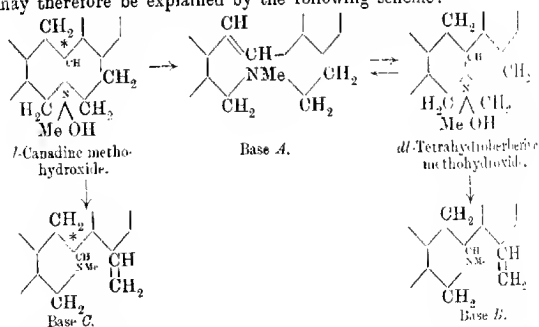


It has now been found that the change takes place in the case of anhydromethylcanadine base *A* with great readiness. After short boiling with aqueous alcohol, this base is converted into a solution of  $\beta$ -tetrahydroberberine methohydroxide, which, when acidified with hydrochloric acid, yields the corresponding methochloride in a yield amounting to 71 per cent. of the theoretical.

It has already been shown that tetrahydroberberine methohydroxide, when evaporated to dryness under atmospheric pressure, yields the base *B*, and it is consequently not surprising to find that the base *A*, when similarly evaporated several times with dilute alcohol, is converted into a mixture of base *B* and the quaternary carbonates.

The disappearance of base *A* when either *l*-canadine or tetrahydroberberine methohydroxides are evaporated on the water-bath under atmospheric pressure, and the formation of the optically inactive base *B* from *l*-canadine, are thus accounted for.

The whole course of the formation of the three anhydro-bases may therefore be explained by the following scheme:



\* An asterisk over the asymmetric carbon atom denotes that the compounds are optically active.

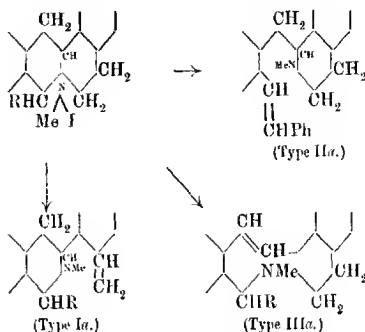
*l*-Canadine methohydroxide, when evaporated either in a vacuum or under atmospheric pressure on the water-bath, yields a small proportion of the optically active base *C* directly; in a vacuum, it yields a large amount of the base *A*, of which a small proportion is converted through tetrahydroberberine methohydroxide into base *B*; under atmospheric pressure, at the water-bath temperature, the whole of *A* is converted into tetrahydroberberine methohydroxide and transformed partly into base *B*, and partly into the quaternary carbonates.

Tetrahydroberberine methohydroxide shows a similar behaviour except that the base *C* cannot be here formed; in a vacuum, a mixture of *A* and *B* is obtained, whilst under atmospheric pressure the only anhydro-base in the final product is *B*. It may be inferred by analogy with the behaviour of *l*-canadine methohydroxide that in the case of tetrahydroberberine methohydroxide a small proportion of base *B* is produced directly in each case.

Applying these results to the work of former investigators, it is clear that Voss and Gadamer's anhydroethylecanadine has, in fact, the constitution which these authors assigned to it. The contention of McDavid, Perkin, and Robinson with respect to its constitution and mode of formation is consequently invalid. The constitution which the latter authors assigned to their anhydro-derivative of tetrahydroberberine benzyl chloride, namely, that of *N*-benzyl-tetrahydroberberine, is, however, doubtless correct, for the conditions of its formation, namely, boiling with alcoholic potassium hydroxide, were such that even if a base of the type of base *A* were primarily produced, it would be converted into a base of the type of base *B*.

It is interesting to note that while these results were being written up for publication there appeared in the *Chemiker Zeitung* of the 4th of March (1913, 27, 270) a report of a paper read by J. Freund before the *Chemische Gesellschaft zu Frankfurt a.M.*, on the 13th December, 1912, in which the degradation of the alkyltetrahydroberberine methiodides is recorded.

The full account of this research has since appeared in the *Annalen* (1913, 397, 1). It is shown that the degradation of alkyl-, arylalkyl-, and aryl-tetrahydroberberine methiodides may take place in different ways:



Where R=benzyl, the anhydro-base was of type IIa, since it yielded hydrastinine on oxidation.

Where R=*isoamyl*, the main product was an anhydro-base, to which the constitution of the type IIIa was assigned, since it behaved similarly to Voss and Gadamer's anhydroethylcanadine. This base was accompanied by small quantities of an isomeric base of type Ia, which could also be prepared by boiling the first base with alcohol. The presence of this second base amongst the products of the degradation appears to be regarded as due to transformation of some of the first base by manipulation.

Where R=phenyl or an alkyl radicle other than *isoamyl*, the single anhydro-base isolated was of type Ia, and the question as to whether this was produced directly or through the intermediate stages of an unstable base of type IIIa changing to the quaternary hydroxide and thence to the isomeride of type Ia, was left open, although it was pointed out that the latter view more readily accounts for the production of a single anhydro-base from the two stereoisomeric racemic forms of  $\alpha$ -alkyltetrahydroberberine hydroxides.

In the light of the present communication it is not surprising that bases of the type of IIIa could not usually be isolated, for the degradation was carried out by boiling with aqueous potassium hydroxide, and it has now been shown that the anhydromethyl canadine of type IIIa is transformed into the base of type Ia at the temperature of boiling water.

It seems probable that the course of the degradation of the  $\alpha$ -alkyltetrahydroberberine methohydroxides is entirely similar to that of tetrahydroberberine methohydroxide as described above, and that a quantitative study of their dehydration in a vacuum would confirm this view.

## EXPERIMENTAL.

*Tetrahydroberberine Methochlorides.*

The methylation of *l*-canadine (Jowett and Pyman, T., 1913, 103, 296) gave a mixture of the  $\alpha$ - and  $\beta$ -methochlorides, of which the latter more sparingly soluble salt was formed in the larger proportion. An experiment was described, showing that the latter was, in fact, the  $\beta$ -salt, that is, the more stable isomeride. Similarly, the methylation of tetrahydroberberine yields two isomeric salts, of which one, the more sparingly soluble, is formed in the larger proportion; the latter is therefore the racemic form of *l*- $\beta$ -canadine methochloride.

Twenty-five grams of tetrahydroberberine and 30 c.c. of methyl iodide were heated for fifteen minutes on the water-bath under a reflux condenser; the excess of methyl iodide was then distilled off, and the residue dissolved in 1.2 litres of boiling water. The solution was then thoroughly agitated with an excess of silver chloride, freed from the silver salts, and evaporated to a volume of about 20 c.c. On cooling, a large quantity of the  $\beta$ -methochloride separated, and this was crystallised from 200 c.c. of hot water, when 5.9 grams of the pure salt were obtained in the first crop. The original mother liquors deposited, after concentration and cooling, a quantity of crude  $\alpha$ -salt, which was also purified by crystallisation from water. The two salts were separated without difficulty, and these were eventually obtained, 19.5 grams of the  $\beta$ -methochloride, and 6.5 grams of the  $\alpha$ -methochloride, both in a pure state. These yields are respectively 60 and 21 per cent. of the theoretical, so that in all 81 per cent. was obtained in a pure state.

$\alpha$ -Tetrahydroberberine methochloride crystallises from water in clusters of colourless, prismatic needles, which contain  $2\text{H}_2\text{O}$ , all of which is lost at  $100^\circ$ . The air-dried salt sinters at  $140^\circ$ , and melts and effervesces at  $141^\circ$  (corr.). After drying at  $100^\circ$ , it melts and effervesces at  $150^\circ$  (corr.). It is soluble in about 30 parts of cold water, and very readily so in hot water:

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{NCl}$  \* lost 0.0184 at  $100^\circ$ .  $\text{H}_2\text{O} = 8.9$ .

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{NCl}$  \* gave 0.3538  $\text{CO}_2$  and 0.0962  $\text{H}_2\text{O}$ .  $\text{C} = 59.5$ ;  $\text{H} = 6.6$ .

$\text{H}_2\text{O}, \text{NCl}, 2\text{H}_2\text{O}$  requires  $\text{C} = 59.2$ ;  $\text{H} = 6.6$ ;  $\text{H}_2\text{O} = 8.5$  per cent.

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{NCl}$  † gave 0.3520  $\text{CO}_2$  and 0.0888  $\text{H}_2\text{O}$ .  $\text{C} = 64.2$ ;  $\text{H} = 6.6$ .

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NCl}$  requires  $\text{C} = 64.7$ ;  $\text{H} = 6.2$  per cent.

$\alpha$ -Tetrahydroberberine methiodide was prepared from the methochloride by double decomposition with potassium iodide and crystallisation from water. It forms warty clusters, which decom-

Air-dried.

†<sub>2</sub> Dried at  $100^\circ$ .

pose at  $251^{\circ}$  (corr.). It is anhydrous, and is sparingly soluble in hot, very sparingly so in cold, water:

0.1430 gave 0.2742  $\text{CO}_2$  and 0.0642  $\text{H}_2\text{O}$ .  $\text{C}=52.3$ ;  $\text{H}=5.0$ .

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NI}$  requires  $\text{C}=52.4$ ;  $\text{H}=5.0$  per cent.

$\beta$ -Tetrahydroberberine methochloride crystallises from water in colourless, well-defined, monoclinic prisms. The air-dried salt shows signs of sintering at about  $180^{\circ}$ , but does not melt and decompose until  $288^{\circ}$  (corr.). It contains  $3\text{H}_2\text{O}$ , of which two are lost at  $100^{\circ}$ , and the remaining one at  $110$ – $120^{\circ}$ . It is soluble in about 80 parts of cold water, but readily so in hot water:

0.3828 \* lost 0.0312 at  $100$ – $110^{\circ}$ .  $\text{H}_2\text{O}=8.2$ .

0.3828 \* „ 0.0448 „  $110$ – $120^{\circ}$ .  $\text{H}_2\text{O}=11.7$ .

0.1495 \* gave 0.3105  $\text{CO}_2$  and 0.0885  $\text{H}_2\text{O}$ .  $\text{C}=56.6$ ;  $\text{H}=6.6$ .

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NCl}\cdot 3\text{H}_2\text{O}$  requires  $\text{C}=56.8$ ;  $\text{H}=6.8$ ;  $2\text{H}_2\text{O}=8.5$ ;  
 $3\text{H}_2\text{O}=12.2$  per cent.

0.1440 † gave 0.3248  $\text{CO}_2$  and 0.0890  $\text{H}_2\text{O}$ .  $\text{C}=61.5$ ;  $\text{H}=6.9$ .

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NCl}\cdot \text{H}_2\text{O}$  requires  $\text{C}=61.8$ ;  $\text{H}=6.4$  per cent.

$\beta$ -Tetrahydroberberine methiodide was prepared from the methochloride by double decomposition with potassium iodide and recrystallisation from water. It forms quadrilateral plates, which decompose at  $248^{\circ}$  (corr.). It is anhydrous, and is sparingly soluble in hot, very sparingly so in cold, water:

0.1472 gave 0.2804  $\text{CO}_2$  and 0.0688  $\text{H}_2\text{O}$ .  $\text{C}=52.0$ ;  $\text{H}=5.2$ .

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NI}$  requires  $\text{C}=52.4$ ;  $\text{H}=5.0$  per cent.

#### *Physiological Action of dl- $\alpha$ - and $\beta$ -Tetrahydroberberine Methochlorides.*

These two salts have been tested by Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, in the same manner as *l*- $\alpha$ - and *l*- $\beta$ -canadine methochlorides (T., 1913, 103, 294). The physiological activities of the two latter salts were previously found to be as 1:12. It has now been found that the ratio of activity of *dl*- $\alpha$ :*dl*- $\beta$ -salt is as 1:4, and of *l*- $\alpha$ :*dl*- $\alpha$  as 1:5. From these data, the activities of *d*- $\alpha$ - and *d*- $\beta$ -canadine methochlorides can be calculated, and the relative activity of the four optically active isomerides is as follows: *l*- $\alpha$ :*d*- $\alpha$ :*l*- $\beta$ :*d*- $\beta$ -canadine methochlorides as 1:9:12:28.

#### *Dehydration of Tetrahydroberberine Methoxydioxide by Evaporation under Atmospheric Pressure: Formation of Base B.*

(1) Ten grams of tetrahydroberberine and 15 c.c. of methiodide were boiled for fifteen minutes on the water-bath under

\* Air-dried.

† Dried at  $100^{\circ}$ .

reflux condenser. The crystalline mass was then heated to remove the excess of methyl iodide, and the residual methiodide dissolved in 500 c.c. of boiling water. The solution was agitated with an excess of silver hydroxide until all the iodide was removed from it and filtered from the silver salts. The resulting solution of the methohydroxide was then evaporated to dryness on the water-bath under atmospheric pressure, when the crude base *B* separated as an insoluble, grey varnish. This was collected and crystallised from alcohol. The alcoholic and aqueous mother liquors were then mixed, and again evaporated to dryness under the same conditions, when a further quantity of the base was obtained. In this way 5.0 grams of base *B*, melting at 111–112°, were obtained. The combined aqueous and alcoholic mother liquors, which no longer gave a separation of insoluble matter on evaporation, were extracted with chloroform, which, however, removed only a trace of material. The liquor was then acidified with hydrochloric acid, when considerable effervescence took place, and 3.2 grams of  $\beta$ -tetrahydroberberine methochloride separated.

(2) It seemed clear from the last experiment that the cause of the low yield of the anhydro-base lay in the combination of a part of the methohydroxide with the carbonic acid of the atmosphere, and this was proved by the following experiment.

Five grams of tetrahydroberberine were converted into a solution of the methohydroxide in 240 c.c. of water in the usual manner, and this solution was then saturated with carbonic acid and evaporated to low bulk. No insoluble, amorphous matter separated during concentration, but a quantity of crystals were obtained in its place, and even after evaporation of the liquor to a thick paste, no insoluble anhydro-base separated. The liquor was then somewhat diluted and set aside to crystallise, the crystals so obtained being again recrystallised from water, when they were found to consist of  $\beta$ -tetrahydroberberine methocarbonate (1.8 grams):

0.1532 \* lost 0.0237 at 100°.  $H_2O = 15.5$ .

$C_{22}H_{29}O_2N \cdot 4H_2O$  requires  $H_2O = 14.8$  per cent.

0.1228 † gave 0.2849  $CO_2$  and 0.0702  $H_2O$ .  $C = 63.3$ ;  $H = 6.4$ .

$C_{22}H_{29}O_2N$  requires  $C = 63.6$ ;  $H = 6.1$  per cent.

This salt, after drying at 100°, melts and effervesces at 165–167° (corr.); it is readily soluble in hot, sparingly so in cold, water. The mother liquors from this salt, on evaporation to dryness with the addition of potassium hydroxide, readily furnished 1.6 grams of base *B*, melting at 112–113°.

(3) Tetrahydroberberine (25 grams) was then converted into a solution of methohydroxide, just as in the first experiment, but

\* Air-dried.

† Dried at 100°.



when the aqueous mother liquors no longer gave a separation of insoluble material on evaporation, potassium hydroxide was added, and a further quantity of the anhydro-base was obtained. Under these conditions 15.7 grams of base *B*, melting at 111–112°, and 4.8 grams, melting at 110–111°, were obtained, the total quantity, 20.5 grams, representing 79 per cent. of the theoretical.

*Dehydration of Tetrahydroberberine Methohydroxide by Evaporation in a Vacuum: Formation of Bases A and B.*

Twenty-five grams of tetrahydroberberine were converted into a solution of the methohydroxide in 1200 c.c. of water, as in the preceding example. This was evaporated to dryness under the diminished pressure effected by a good water-pump, the bolt-head containing the solution being placed in a vigorously boiling water-bath. The product was heated under these conditions for a further thirty minutes after it appeared to be dry. The residue was then boiled with 100 c.c. of ethyl acetate, which had been well dried over anhydrous potassium carbonate, and filtered from a very small amount of insoluble matter. The filtrate deposited, on cooling, a large quantity of the base *A* in colourless, silky needles, melting at 132–133°; the mother liquor from these, on concentration to about half volume and cooling, gave a further crop of the same melting point. The two crops together amounted to 13.0 grams. The ultimate mother liquor was evaporated to dryness, and the residual mixture of bases separated by means of the different solubilities of the hydrochlorides.

The residue was ground with 100 c.c. of hot 3 per cent. aqueous hydrochloric acid, which separated the mixture into hydrochlorides easily soluble, and nearly insoluble in hot dilute hydrochloric acid. The acid solution was filtered from the insoluble hydrochlorides, and the latter well washed with hot aqueous 1 per cent. hydrochloric acid; the filtrate and washings were then combined, rendered alkaline with ammonia, and extracted with ether. The ethereal solution, after being dried and distilled to a volume of a few c.c., deposited on cooling 1.1 grams of base *A*, melting at 132–133°, whilst the filtrate from these crystals gave, on evaporation to dryness, 0.9 gram of partly crystalline material. The total yield of base *A*, 14.1 grams, is 54 per cent. of the theoretical.

The insoluble hydrochlorides were shaken with ammonia and ether, and the ethereal solution was evaporated to dryness and dissolved in a little alcohol. On keeping, 5.0 grams of base *B*, melting at 111–112°, were collected, and the mother liquor contained only 0.3 gram of amorphous substances.

The yield of base *B*, 5.0 grams, is 19 per cent. of the theoretical.

*Dehydration of L-canadine Methohydroxide by Evaporation under Atmospheric Pressure: Formation of Bases B and C.*

(1) Ten grams of L-canadine were converted into a solution of the methohydroxides in water in the usual manner.\* This solution, amounting in volume to about 500 c.c., was evaporated to dryness in the water-bath under atmospheric pressure; the residue was diluted with water, and the separated clear, grey varnish crystallised from a quantity of alcohol just sufficient to dissolve it when hot; on cooling, the first crop of crystals separated. The aqueous and alcoholic mother liquors were then combined, again evaporated to dryness, and subjected to the same treatment once more, yielding the second crop of crystals. The aqueous and alcoholic mother liquors from the second crop were then combined and again evaporated to dryness when very little insoluble matter separated, since the compound was now present in the form of methyl carbonate owing to combination with the carbonic acid of the atmosphere. A quantity of 10 per cent. aqueous potassium hydroxide was added, and evaporation to low bulk was repeated twice, when a further quantity of base insoluble in water was formed. After crystallisation from a little alcohol, this formed the third crop.

The amounts and properties of the three crops were as follows:

	Grams.	M. p.	[ $\alpha$ ] <sub>D</sub>
1st crop .....	3.3	105–110°	–41.9°
2nd „ .....	1.5	105–111	–19.8
3rd „ .....	2.7	111–113	–3.3

Fractional crystallisation from ethyl acetate of these crops, together with those of the second experiment described below, gradually effected a separation into substances of low and high rotation, the latter being more readily soluble. After repeated

\* The mixture of  $\alpha$ - and  $\beta$ -methohydroxides obtained in this way was always employed for the dehydration. The possibility that the two compounds might behave differently had been tested in the preliminary experiments in the case of evaporation on the water-bath (this vol., p. 299). It was there stated that 10 grams of L-canadine methiodide gave 4.1 grams of anhydro-base, melting at 111–112°, and having [ $\alpha$ ]<sub>D</sub> = 25.2° (after one crystallisation from alcohol). This yield is 56 per cent. of the theoretical. It was further stated that a similar result was obtained, starting from L- $\beta$ -canadine methochloride; the details of the latter case are as follows:

Eight grams of hydrated L- $\beta$ -canadine methochloride gave 2.3 grams of anhydro-base, melting at 111–112°, and having [ $\alpha$ ]<sub>D</sub> = 24.0° (after one crystallisation from alcohol). This yield is 49 per cent. of the theoretical.

The anhydro base obtained in these experiments was, of course, a mixture of the anhydro-bases B and C; the above results indicate that they are produced in approximately the same proportion, whether the  $\alpha$ - or  $\beta$ -metho-salts are employed.

crystallisations, the most sparingly soluble fraction was obtained almost free from optical activity ( $[\alpha]_D -0.3^\circ$ ), when it melted at  $114-115^\circ$  (corr.), and was found to represent the base  $\beta$  in a nearly pure state:

0.1526 gave 0.3994  $\text{CO}_2$  and 0.0890  $\text{H}_2\text{O}$ .  $\text{C}=71.4$ ;  $\text{H}=6.5$ .  
 $\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}$  requires  $\text{C}=71.4$ ;  $\text{H}=6.6$  per cent.

The purification of the more readily soluble portion was more difficult, and the quantity of material was insufficient to admit of complete purification, but an end-fraction, melting at  $99-101^\circ$  and having  $[\alpha]_D -99^\circ$ , was obtained, consisting mainly of base  $C$ , which it is subsequently shown melts at  $101-102^\circ$  (corr.), and has  $[\alpha]_D -113.6^\circ$  when pure. No evidence of the presence of a third constituent of the mixture was obtained, and it is therefore admissible to calculate the proportion of two bases in the mixture from the known specific rotations of  $B$  and  $C$ .

The yields thus calculated are 57 per cent. of the theoretical of  $B$ , and 15 per cent. of  $C$ .

(2) Twenty-five grams of *l*-canadine were then converted into the methohydroxide, but in order to avoid contact with the carbonic acid of the atmosphere as far as possible, the solution was evaporated on the water-bath in a vacuum to a volume of about 200 c.c. It was then transferred to an evaporating dish, the small amount of base that had separated on the sides of the vessel being washed in with a little alcohol, and the evaporation to dryness continued under atmospheric pressure. The resulting product was then treated as in the previous case, two crops being collected before, and one after, the addition of potassium hydroxide. They were:

	Grams.	M. pt.	$[\alpha]_D$
1st crop .....	16.6	109-111	24
2nd „ .....	1.5	108-110	33
3rd „ .....	1.2	111-112	8

The yields of the two bases calculated from these figures are: Base  $B$ , 71 per cent. of the theoretical; base  $C$ , 11 per cent. of the theoretical.

*Dehydration of l-Canadine Methohydroxide by Evaporation in a Vacuum: Formation of Bases A, B, and C.*

Thirty grams of *l*-canadine were converted into a solution of the methohydroxide in 1500 c.c. of boiling water in the usual manner. The solution was then evaporated to dryness under the diminished pressure effected by a good water-pump, the bolt-head containing the solution being placed in a vigorously boiling water-bath, and

the residue was heated under these conditions for a further thirty minutes after it appeared to be dry.

The residue was then boiled with about 100 c.c. of ethyl acetate, which had been well dried over anhydrous potassium carbonate, and filtered from a very small amount of insoluble matter. The filtrate, on cooling, deposited a large quantity of the base *A* in colourless, silky needles, melting at 133°; the mother liquor from these, on concentration to about half volume and cooling, gave a further crop, melting at 131°. The two crops together amounted to 14.8 grams.

The ultimate ethyl acetate mother liquor, after concentration to very low bulk, gave about 8 grams of a mixture of bases, melting at 85–95°, and a residue of 2.5 grams of gummy bases.

These last two fractions were ground with 100 c.c. hot 3 per cent. aqueous hydrochloric acid, which separated the mixture into hydrochlorides soluble and nearly insoluble in hot dilute hydrochloric acid.

The acid solution was filtered from the insoluble hydrochlorides, and the latter well washed with hot very dilute hydrochloric acid; the filtrate and washings were then combined, rendered alkaline with ammonia, and extracted with ether. The ethereal solution, after being dried and distilled to a volume of a few c.c., deposited, on cooling, 1.9 grams of the base *A*, melting at 133°, the filtrate from this on evaporation to dryness amounting to only 0.8 gram of partly crystalline material.

The total yield of the nearly pure base *A* thus amounts to 16.7 grams, that is, 53 per cent. of the theoretical.

The insoluble hydrochlorides were shaken with ammonia and ether, and the ethereal solution was evaporated to low bulk and kept, when crystals separated; the mother liquor, on concentration, deposited a further quantity of crystals, and eventually the following fractions were obtained in the order given:

Grams.	M. p.	$[\alpha]_D$
3.0	105.7	- 72
1.5	102	98
0.5	98	- 101
0.2	residue	

In a second experiment, using 50 grams of *L*-canadine, the similar fractions obtained were:

Grams.	M. p.	$[\alpha]_D$
5.7	102–106	60
3.4	100–102	83

The fractions from these two experiments and from a preliminary experiment, in all 18.9 grams, with specific rotatory power from

$-30^{\circ}$  to  $-101^{\circ}$ , were suitably combined, and crystallised fractionally from ethyl acetate. By this means a gradual separation was effected, and at a certain stage, for instance, 8.0 grams, melting at  $111-113^{\circ}$  and having  $[\alpha]_D -18.6^{\circ}$ , were obtained as the most sparingly soluble portion, and 5.7 grams in small fractions, melting at about  $100^{\circ}$  and having  $[\alpha]_D$  from  $-103^{\circ}$  to  $-108^{\circ}$  as the most readily soluble portion.

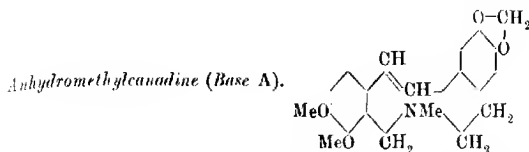
The first of these fractions after two crystallisations from 25 c.c. of alcohol amounted to 4.3 grams with  $[\alpha]_D -11.3^{\circ}$ , and after two further crystallisations from ethyl acetate to 2.0 grams with  $[\alpha]_D -2.4^{\circ}$ ; after two further crystallisations from ethyl acetate, 0.6 gram with  $[\alpha]_D -2.3^{\circ}$  was obtained. In spite of the constancy obtained in the specific rotatory power, there is little reason to doubt that this more sparingly soluble fraction consists mainly of the inactive base *B*. It melted at the same temperature, namely,  $114-115^{\circ}$  (corr.), did not depress the melting point of the latter, and had the same general properties.

The later fraction, which was readily soluble in cold ethyl acetate, was crystallised from a mixture of this solvent (1 part) with alcohol (3 parts), when fractions of somewhat lower rotation separated at first; on concentrating the mother liquors and cooling, fractions of higher rotation crystallised. The latter were crystallised in a similar manner, until of almost constant specific rotatory power, and eventually furnished a small quantity of the base *C* with  $[\alpha]_D -113.6^{\circ}$ .

Whilst this product is regarded as very nearly pure, it must be pointed out that the purification of a substance which tends to remain in the mother liquors is necessarily difficult, and it may be that a repetition of this experiment with still larger quantities might result in the isolation of base *C* with a slightly higher specific rotatory power.

No evidence was obtained during the fractionation of the presence of a constituent other than *B* or *C*, and it is therefore admissible to calculate the proportion of the two bases in the original mixture, assuming that *B* is optically inactive, and that *C* has  $[\alpha]_D -113.6^{\circ}$ .

It is thus found that the crystalline fractions from the first experiment, 5.1 grams, amounted to 1.4 grams of *B*, that is, 4 per cent., and 3.7 grams of *C*, that is, 12 per cent. of the theoretical; whilst in the second experiment the total quantity (8.6 grams) represents 2.8 grams of *B*, that is, 5 per cent., and 5.8 grams of *C*, that is, 11 per cent. of the theoretical.



This base is the chief product of the dehydration of *l*-canadine and tetrahydroberberine methohydroxide by evaporation to dryness in a vacuum, and is formed in a yield amounting to about 53 per cent. of the theoretical. It crystallises from anhydrous ethyl acetate in colourless, woolly needles, which melt at 135–136° (corr.). It suffers no loss at 100°, and is optically inactive:

0.1556 gave 0.4058 CO<sub>2</sub> and 0.0920 H<sub>2</sub>O. C = 71.1; H = 6.6.

0.1676 „ 0.4370 CO<sub>2</sub> „ 0.0994 H<sub>2</sub>O. C = 71.1; H = 6.6.

C<sub>21</sub>H<sub>25</sub>O<sub>4</sub>N requires C = 71.4; H = 6.6 per cent.

Molecular-weight determination by the cryoscopic method:

0.2096 in 18.56 benzene gave  $\Delta t$  = -0.170°. M.W. = 332.

0.5624 „ 18.56 „ „  $\Delta t$  = -0.440°. M.W. = 352.

C<sub>21</sub>H<sub>25</sub>O<sub>4</sub>N requires M.W. = 353.

It is insoluble in water, sparingly soluble in cold alcohol, ethyl acetate, or ether, and readily so in chloroform or hot ethyl acetate.

It is decomposed by hot alcohol. The cold alcoholic solution reacts faintly alkaline to litmus, but after heating this solution for a few minutes on the water-bath, the solution reacts strongly alkaline owing to the formation of tetrahydroberberine methohydroxide. The readiness with which this conversion takes place is illustrated by the following experiment.

Three grams of the pure base were dissolved in 30 c.c. of hot alcohol, and 30 c.c. of water were added; the alcohol was then distilled from the solution, leaving it slightly turbid. A further quantity of 10 c.c. of alcohol, followed by 20 c.c. of water, was next added, and the alcohol again removed by distillation. The solution was then filtered from a very small quantity of insoluble amorphous matter, and acidified with concentrated hydrochloric acid. On cooling, 2.8 grams of  $\beta$ -tetrahydroberberine methochloride separated in a pure state, that is, 71 per cent. of the theoretical yield. This salt was identified as such by its melting point, crystalline form, sparing solubility in water, and inability to decolorise potassium permanganate. The mother liquor from this salt did not appear to contain any of the  $\alpha$ -methochloride.

Anhydromethylcanadine (Base A) is also decomposed on heating with chloroform. A solution of 1 gram in 25 c.c. of chloroform was evaporated to a syrup and kept, when the residue set to a

crystalline mass having a high melting point. After extracting this with a little hot water, the filtered extract deposited crystals, which were again recrystallised from water, and then represented 0.6 gram of pure  $\beta$ -tetrahydroberberine methochloride.

Base *A* decolorises bromine in chloroform, yielding a colourless solution, and decolorises potassium permanganate in aqueous acid solution.

The *hydrochloride* of base *A* was obtained as follows:

Two grams of the base were added to 10 c.c. of hot 5 per cent. hydrochloric acid, and the solution cooled, when the aqueous salt separated in rosettes of colourless plates. This salt sintered somewhat at 150–155° (corr.), but did not melt until 288° (corr.), being probably converted into  $\beta$ -tetrahydroberberine methochloride under the influence of heat:

0.1760 \* lost 0.0176 at 100°.  $H_2O = 10.0$ .

0.1472 † „ 0.3356  $CO_2$  and 0.0860  $H_2O$ .  $C = 62.2$ ;  $H = 6.5$ .

$C_{21}H_{23}O_4N, HCl, 3\frac{1}{2}H_2O$  requires loss of  $2\frac{1}{2}H_2O = 9.9$  per cent.

$C_{21}H_{23}O_4N, HCl, H_2O$  requires  $C = 61.8$ ;  $H = 6.4$  per cent.

This salt is readily soluble in hot, sparingly so in cold, water. Freshly made solutions of this salt in water gave with ammonia a white precipitate, at first amorphous, then crystalline, of the original base *A*, and decolorised aqueous potassium permanganate. An aqueous solution of the salt, after digestion for a short time in the water-bath, no longer gave a turbidity with ammonia nor decolorised potassium permanganate, owing to the conversion of the salt into  $\beta$ -tetrahydroberberine methochloride.

The *methiodide* of base *A* was prepared by heating the latter with methyl iodide for a few minutes on the water-bath. It crystallises from alcohol in colourless plates containing  $EtOH$ , which begin to turn brown at about 220°, and to sinter and effervesce at 225° (corr.). It is sparingly soluble in cold water or alcohol, but fairly readily so in hot water. It decolorises potassium permanganate in aqueous solution:

0.1721 lost 0.0045 at 120°.  $EtOH = 2.6$ .

0.1676 † gave 0.3276  $CO_2$  and 0.0848  $H_2O$ .  $C = 53.3$ ;  $H = 5.7$ .

$C_{20}H_{20}O_4NI$  requires  $C = 53.1$ ;  $H = 5.3$  per cent.

*Conversion of Base A into Base B.*—Since the base *A* is easily converted into tetrahydroberberine methohydroxide, and this readily yields the base *B* on evaporation under atmospheric pressure, the conversion of base *A* into base *B* can be readily effected.

\* Two grams of base *A* were dissolved in 10 c.c. of hot alcohol, and 10 c.c. of water added. The liquor was evaporated nearly to dryness

\* Air-dried.

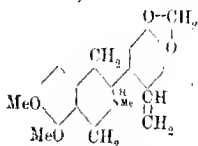
† Dried at 100°.

‡ Dried at 120°.

on the water-bath under atmospheric pressure, and the residue again dissolved in a little alcohol, diluted with water, and again evaporated to dryness. The residue was then mixed with a little hot water, and the insoluble varnish collected and crystallised from alcohol, when 0.75 gram of base *B*, melting at 111–112°, was obtained.

*Anhydromethylecanadine (Base B).*

*dl-N-Methylisotetrahydroberberine,*



This base is the sole anhydro-base produced by the evaporation of an aqueous solution of tetrahydroberberine methohydroxide under atmospheric pressure, the yield amounting to 79 per cent. of the theoretical, when potassium hydroxide is employed to decompose the methocarbonates formed at the same time. It is also formed in 19 per cent. yield, when the same compound is evaporated in a vacuum, and is further obtained mixed with the *levo*-variety by the degradation of *L*-canadine methohydroxide. This base crystallises from alcohol in tufts of small, colourless needles, which melt at 114–115° (corr.). It is anhydrous, and is insoluble in water, sparingly soluble in cold, but readily so in hot, alcohol, fairly readily soluble in cold, and very readily so in hot, ethyl acetate, fairly readily soluble in ether, and readily so in chloroform:

0.1598 gave 0.4183 CO<sub>2</sub> and 0.0940 H<sub>2</sub>O. C = 71.4; H = 6.6.

C<sub>21</sub>H<sub>23</sub>O<sub>4</sub>N requires C = 71.4; H = 6.6 per cent.

Molecular-weight determination by the ebullioscopic method:

0.1824, in 23.28 chloroform, gave  $\Delta t$  0.072°. M.W. = 398.

0.4012, „ 23.28 „ „  $\Delta t$  0.185°. M.W. = 341.

0.4978, „ 23.28 „ „  $\Delta t$  0.213°. M.W. = 322.

C<sub>21</sub>H<sub>23</sub>O<sub>4</sub>N requires M.W. = 353.

This base is optically inactive. An alcoholic solution reacts faintly alkaline to moist litmus paper, and does not become more alkaline after boiling on the water-bath. It decolorises bromine in chloroform, yielding a nearly colourless solution with a faint green tinge, and decolorises potassium permanganate in aqueous acid solution. This base and its salts are not converted into tetrahydroberberine methohydroxide and metho-salts in the various circumstances in which base *A* and its salts are so converted.

The *hydrochloride* was prepared by adding dilute aqueous hydro-



chloric acid to an alcoholic solution of the base, when it separated in white, matted, woolly needles, which decompose at  $258^{\circ}$  (corr.). It is anhydrous, and is very sparingly soluble in cold water or alcohol, more readily so in these solvents when hot. It is very sparingly soluble in hot dilute hydrochloric acid:

0.1468 gave 0.3470  $\text{CO}_2$  and 0.0778  $\text{H}_2\text{O}$ .  $\text{C} = 64.4$ ;  $\text{H} = 5.9$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N} \cdot \text{HCl}$  requires  $\text{C} = 64.7$ ;  $\text{H} = 6.2$  per cent.

The *methindide* was prepared by heating the base with methyl iodide on the water-bath for a few minutes. It crystallised from alcohol in colourless, anhydrous plates, which melted sharply at  $231^{\circ}$  (corr.). It is very sparingly soluble in cold, more readily so in hot, water or alcohol. It decolorises potassium permanganate in aqueous solution:

0.1820 gave 0.3562  $\text{CO}_2$  and 0.0852  $\text{H}_2\text{O}$ .  $\text{C} = 53.4$ ;  $\text{H} = 5.2$ .

$\text{C}_{22}\text{H}_{26}\text{O}_4\text{N}$  requires  $\text{C} = 53.3$ ;  $\text{H} = 5.3$  per cent.

#### *Anhydromethylcanadine (Base C).*

##### *1-N-Methylisotetrahydroberberine.*

This base is produced in a yield of about 12 per cent. by the dehydration of *l*-canadine methohydroxide either under atmospheric pressure or in a vacuum. It crystallises from alcohol in clusters of clear, colourless prisms, which melt at  $101\text{--}102^{\circ}$  (corr.). It is anhydrous and is insoluble in water, somewhat sparingly soluble in cold, but readily so in hot, alcohol, readily soluble in cold, and very readily so in hot, ethyl acetate, and readily soluble in ether or chloroform:

0.1517 gave 0.3986  $\text{CO}_2$  and 0.0913  $\text{H}_2\text{O}$ .  $\text{C} = 71.6$ ;  $\text{H} = 6.7$ .

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}$  requires  $\text{C} = 71.4$ ;  $\text{H} = 6.6$  per cent.

The specific rotatory power was determined in chloroform solution:

$$\alpha_D - 2.30^{\circ}; c = 1.012; l = 2 \text{ dm.}; [\alpha]_D = 113.6^{\circ}.$$

An alcoholic solution reacts faintly alkaline to moist litmus paper and does not become more alkaline after boiling on the water-bath. It decolorises bromine in chloroform, yielding a nearly colourless solution with a faint green tinge, and decolorises potassium permanganate in aqueous acid solution. This base and its salts are not converted into tetrahydroberberine methohydroxide and metho salts in the various circumstances in which base A and its salts are so converted.

The *hydrochloride* was prepared in the same manner as the salt of the racemic base. It separated in tufts of woolly needles, which melted at  $229^{\circ}$  (corr.). It is very sparingly soluble in cold water.

sparingly so in hot water or cold alcohol, and fairly readily so in hot alcohol. It is very sparingly soluble in hot dilute hydrochloric acid:

0.1497 gave 0.3565  $\text{CO}_2$  and 0.0836  $\text{H}_2\text{O}$ .  $\text{C}=61.9$ ;  $\text{H}=6.2$ .

$\text{C}_{27}\text{H}_{23}\text{O}_4\text{N}_2\text{IICl}$  requires  $\text{C}=61.7$ ;  $\text{H}=6.2$  per cent.

The *methiodide* crystallises from alcohol in colourless plates, which melt at  $230^\circ$  (corr.). It is anhydrous, and is sparingly soluble in cold water or alcohol. It decolorises potassium permanganate in aqueous solution:

0.1687 gave 0.3310  $\text{CO}_2$  and 0.0805  $\text{H}_2\text{O}$ .  $\text{C}=53.5$ ;  $\text{H}=5.3$ .

$\text{C}_{22}\text{H}_{20}\text{O}_4\text{NI}$  requires  $\text{C}=53.4$ ;  $\text{H}=5.3$  per cent.

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### LXXXV.—*Optical Activity and Enantiomorphism of Molecular and Crystal Structure.*

By THOMAS VIPOND BARKER and JAMES ERNEST MARSH.

THE view may be regarded as axiomatic that the property of optical activity is wholly restricted to substances possessing an enantiomorphous structure, that is, a structure which is non-superposable with its mirror image. It is convenient to divide optically active substances into two classes: first, those in which the rotatory power is limited to the crystalline state of aggregation, as, for example, quartz; secondly, those in which the activity persists when the crystalline structure is destroyed by dissolving, liquefying, or vaporising the substance, for example, seignette salt, camphor, and turpentine. The prevailing view concerning these two classes is that in the first the seat of the activity lies in an enantiomorphous, spiral grouping of the molecules in the crystal edifice, which breaks down on dissolution, whilst in the second class the activity is referred to an enantiomorphous configuration of the atoms within the chemical molecule, which configuration is independent of the state of aggregation.

The objects of the present paper are: first, to point out that the theory of crystal structure is incapable of accounting for the activity of many substances of the first class by a spiral grouping of molecules, from which it follows that the molecular configuration must be enantiomorphous in the same sense as is recognised for substances of the second class; secondly, to indicate for such sub-

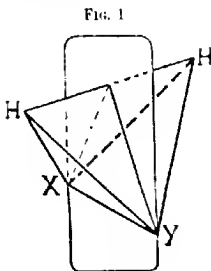
stances chemical constitutions of an enantiomorphous character which seem to be in harmony with the general chemical behaviour of the substances concerned.

Before proceeding to the main theme it will be necessary to discuss separately the general nature of molecular and crystal structure which shall exhibit enantiomorphism.

*Conditions Necessary for Optical Activity of Molecular Structure.*

In the simpler carbon compounds the essential difference between an enantiomorphous configuration and one which is superposable with its mirror image is that the latter possesses a plane of symmetry, for example,  $\text{CH}_2\text{XY}$  possesses a plane of symmetry, whereas  $\text{CHXYZ}$  does not, and is, in fact, enantiomorphous. In view of the enormous number of compounds of these types which have been investigated, it is not surprising that chemists came to the conclusion that any structure devoid of a plane of symmetry is necessarily enantiomorphous. This is erroneous. The complete conditions for geometrical enantiomorphism have been long recognised by crystallographers, and are three in number: the molecular configuration must not only be devoid of (1) a plane of symmetry, but also (2) of a centre of symmetry, and (3) of an alternating axis of symmetry. The presence of any one of these three elements of symmetry suffices to render a configuration superposable with its mirror image. The precise meanings of these three terms will now be explained and illustrated by concrete examples.

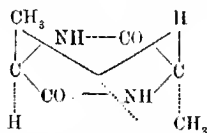
*Plane of Symmetry.*—When a configuration can be divided into



two halves so that the reflection of one half across a mirror, placed in contact with the plane of the section, restores the missing half, there is a plane of symmetry. Thus, in a disubstituted product of methane,  $\text{CH}_2\text{XY}$ , there is a plane of symmetry cutting the C, X, and Y atoms into equal halves, and each hydrogen atom is symmetrically

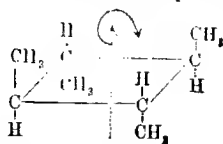
disposed on opposite sides of the plane. Although containing no other symmetry, the substance is superposable with its mirror image, and therefore is incapable of existence in optically active forms.

*Centre of Symmetry.*—This involves similarity about the centre of the molecule in the following sense: lines drawn through the centre of the whole molecule to each and every atom meet a similar atom when produced in the opposite direction. Thus, in *trans*-1:4-diketo-2:5-dimethylpiperazine (alanyl anhydride) any line drawn through the centre of the ring to any atom (either above, below, or in the ring) meets a similar atom similarly environed, when produced backwards. In the figure given, lines have been



drawn connecting pairs of *trans*-hydrogen atoms and methyl groups to indicate the symmetry about the centre ("centrosymmetry") by the presence of which optical activity is precluded (E. Fischer, *Ber.*, 1906, 39, 467, 3981).

*Alternating Axis of Symmetry.*—This peculiar element of symmetry is illustrated by, say, 1:3-*cis*-2:4-*trans*-tetramethylcyclohexane. If any hydrogen atom or methyl group be rotated through an angle of  $90^\circ$  about the vertical axis indicated, and then reflected across the horizontal plane (that is, the plane perpendicular to the



axis of rotation), it comes into superposition with a corresponding hydrogen atom or methyl group, and the same is true of the molecule as a whole. The similar atoms or groups are seen to alternate successively above and below the plane of reflection; hence the term alternating. The molecule is superposable with its mirror image by virtue of the alternating axis of symmetry.

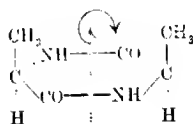
In the illustration just given there are evidently two vertical planes of symmetry cutting diagonally through the ring carbon atoms, and it might be objected that the presence of these two planes of symmetry are in reality the cause of the superposability. However, the methyl groups be replaced alternately by the groups XYZ and CXZY, there would be no longer any planes of

symmetry, and the molecule, although possessing no less than eight asymmetric carbon atoms, would be an inactive, internally compensated compound by virtue of the alternating axis of symmetry which would, in fact, be the sole element of symmetry.

In configurations possessing alternating axes of symmetry, the successive rotations must be  $360^\circ/n$ , where  $n$  is an even number. When  $n=2$ , the alternating axis is equivalent to a centre of symmetry; where  $n=6, 10, 14$ , etc., the alternating axis also involves a centre of symmetry, but where  $n=4$  (as above), 8, 12, etc., this does not hold.

In testing a new configuration as to the elements of symmetry actually present, it must be understood that in the case of single linkings the atoms or groups must be rotated into as symmetrical positions as possible, since experience has proved that atoms or groups invariably take up such a symmetrical, favourable configuration by virtue of free rotations about single linkings.

Although an enantiomorphous configuration must be devoid of all the three elements discussed, it need not necessarily be totally devoid of symmetry, that is, asymmetric in the literal sense. For example, the *cis*-form of 1:4-diketo-2:5-dimethylpiperazine, although optically active, possesses an ordinary (as opposed to alternating)



axis of symmetry. It is seen that by simply rotating the whole molecule through  $180^\circ$  about the axis indicated, each atom comes into congruence with a similar atom, and the molecule as a whole presents the same aspect before and after the rotation. The above axis is termed digonal, because the rotation is  $360^\circ/2$ . Substances can be easily formulated exhibiting trigonal (rotation:  $360^\circ/3$ ), tetragonal, pentagonal, etc., axes of symmetry, of a enantiomorphous character.

It is almost needless to add that in every case where the constitution of a substance, exhibiting optical activity in the non-crystalline condition, has been established, the molecular configuration is devoid of plane, centre, and alternating axis of symmetry. For example, the two optically active forms of tartaric acid are configurationally devoid of all symmetry whatsoever. The internally compensated meso-form has either a plane of symmetry or a centre of symmetry, according as to which of the two possible favourable configurations is taken up by the molecule by virtue



mentioned are known respectively as tetragonal, digonal, trigonal, and hexagonal.

The character of the digonal screw axis is especially important for the present subject. By a rotation of the point  $P_1$  through  $180^\circ$ , followed by a translation equal to half  $P_1P_3$ , the point  $P_3$  is located, and a subsequent operation discovers the point  $P_5$ . Now the points  $P_3$  and  $P_5$  are successively obtained, no matter in which direction the rotation is effected; there is no physical difference, then, between a rotation of  $+180^\circ$  and one of  $-180^\circ$ , and the two arrangements are no longer distinguishable by an enantiomorphous, spiral nature. Any assemblage of points possessing no other screw axes save digonal can only be endowed with optical activity providing the points themselves (that is, the molecules) are enantiomorphous.

Crystals belonging to the rhombic, monoclinic, and triclinic systems cannot possess screw axes other than digonal. Again, in the sodium chlorate class of the cubic system, although the point-assemblages exhibit trigonal screw axes, the latter are always paired, each  $d$ -spiral being accompanied by a  $l$ -spiral axis. Now optical activity has been recorded in three rhombic, three monoclinic, and four substances having the symmetry of sodium chlorate. Among these ten cases there are four which admittedly have an enantiomorphous molecular configuration, namely, seignette salt, sucrose, rhamnose, and tartaric acid. The remaining six substances, which must equally possess enantiomorphous configurations, are: magnesium sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ; Schlippe's salt,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ ; sodium uranyl acetate,  $\text{Na}_2\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$ ; sodium chlorate and sodium bromate.

#### *Co-ordination and Valency.*

The work of Werner and the views expressed by him on his theory of co-ordination seem to show that whilst the co-ordination number of an element is not the same as its valency, yet, like valency, it is constant for a large series of compounds, and the atoms or groups associated in co-ordination with the element have themselves a monad or dyad character. Thus, the groups  $\text{Cl}$ ,  $\text{NO}_2$ ,  $\text{OH}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  are monad, whilst the groups  $\text{C}_2\text{H}_4(\text{NH}_2)_2$ ,  $\text{CO}_3$ ,  $\text{C}_2\text{O}_4$  are dyad. In this way the co-ordination number for cobalt is six, no matter whether it be associated with six  $\text{NH}_2$ -groups or with three ethylenediamine groups. It seems therefore likely that the oxygen atom will have double the co-ordination value of that of chlorine, hydroxyl, or  $\text{NO}_2$ , just as it has double the valency value. It will follow therefore that in the groups  $(\text{ClO}_2)'$ ,  $(\text{NO}_3)'$ ,  $(\text{CO}_3)''$ , the co-ordination number of  $\text{Cl}$ ,  $\text{N}$ , and  $\text{C}$  will be six, and

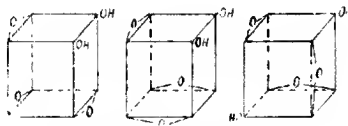
the co-ordination figure will be an octahedron, each oxygen atom being represented as attached to two adjacent corners of the octahedron. Again, in the groups  $\text{OsO}_4$ ,  $(\text{ClO}_4)'$ ,  $(\text{SO}_4)''$ ,  $(\text{PO}_4)'''$ ,  $(\text{SiO}_4)''''$ , the co-ordination number will be eight, and the co-ordination figure a cube, where each oxygen atom influences, or is attached to, two adjacent corners.

*Constitution of Substances with Co-ordination Number Eight.*

To this category belong all the substances previously mentioned excepting sodium chlorate and bromate. The constitutions suggested will be best illustrated by treating the heptahydrated magnesium sulphate in some detail.

*Magnesium Sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .*—This salt loses six molecules of water of crystallisation much more easily than the seventh, which requires a temperature of  $200^\circ$ . Again, the naturally occurring monohydrated salt, kieserite, requires prolonged boiling with water before it will dissolve. There appears, then, every good reason for supposing that one of the seven molecules of water is water of constitution, and is presumably bound to the acidic portion of the molecule, with the result that one of the doubly co-ordinated oxygen atoms is developed and forms two hydroxyl groups; the constitution may therefore be written  $[\text{SO}_4 \cdot 2\text{OH}]\text{Mg} \cdot 6\text{H}_2\text{O}$ . Now there are three possible special formulæ for the co-ordinated portion of the molecule:

FIG. 3.



In the first two formulæ the hydroxyl groups occupy *cis*-positions, but in the third formula, *trans*-positions. The first formula possesses two planes of symmetry, the second, a single plane of symmetry; so neither is of an enantiomorphous character. The third *trans*-formula, although possessing a trigonal axis of symmetry, has neither plane, centre, nor axis of alternating symmetry, and is consequently non-superposable with its mirror image. It is accordingly suggested that the *trans*-formula represents the stereochemical constitution of the acidic radicle of magnesium sulphate, and confers enantiomorphism on the molecule as a whole. Since in solution the magnesium is separately ionisable, it lies of necessity outside the co-ordination sphere of the sulphur, and it appears



reasonable to suppose that it is in turn co-ordinatively surrounded by the six molecules of water of crystallisation.

*Sodium Dihydrogen Phosphate,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ .*—The constitution of this compound would appear to be analogous to that of the foregoing, namely,  $[\text{PO}_3 \cdot 2\text{OH}]\text{NaH}_2$ , in which, as before, the hydroxyl groups occupy the *trans*-position.

*Schlippe's Salt,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ .*—No data exist concerning a possible division of the water into water of constitution and of crystallisation. Enantiomorphous formulæ are, indeed, obtainable by taking one, two, three, or four molecules as water of constitution, each molecule forming with a corresponding double bond sulphur atom the groups  $\text{SH}$  and  $\text{OH}$ . The number of possible spacial formulæ are respectively: one active and one inactive, four active and four inactive, two active and two inactive, one active and four inactive. In view of this, it is impossible to indicate any particular formula for this salt.

*Sodium Urange Acetate,  $\text{NaUO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$ .*—If, as seems likely, the sodium atom be supposed to lie outside the co-ordination sphere of the uranium, the co-ordination number of the latter becomes seven, and it becomes impossible to indicate, a priori, any likely configuration. If, on the other hand, the unlikely assumption be made that the sodium makes up the eighth co-ordination number, the number of possible spacial formulæ can be easily worked out and proves to be four—three active and one inactive.

#### *Collateral Evidence in Favour of the Constitutions Suggested.*

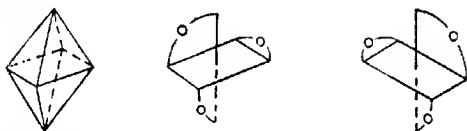
The constitutions which have been suggested for the first two compounds discussed are based fundamentally on the assumption that a certain amount of water of constitution is included in the acidic part of the molecule, and confers on it enantiomorphism. Now there are, as a matter of fact, two possible spacial formulæ for the anhydrous group  $(\text{SO}_4)$ , both of which possess planes of symmetry; with neither of these possible configurations, then, would optical activity be expected. This expectation is fully in accordance with the facts, for there is only one case known of optical activity amongst the large class of anhydrous sulphates, orthophosphates, orthosilicates, periodates, perruthenates, etc., namely, potassium lithium sulphate,  $\text{KLiSO}_4$ . This substance crystallises in the hexagonal system in a class which admits of the presence of hexagonal screw axes, and accordingly even in this case no enantiomorphism of molecular configuration is called for.

The lowering of the symmetry of the molecular configuration by the presence of a molecule of water of crystallisation is of quite frequent occurrence, as is evidenced by the appearance of mono-

hydrated salts in enantiomorphous forms. Thus, the monohydrated lithium sulphate,  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ , is one of the classical examples of enantiomorphism in the monoclinic system. The proof of the presence of optical activity in such a crystal is a somewhat laborious process, since the rotatory power can only be observed in two sections, which have to be ground with great accuracy. It is proposed to undertake this work when the necessary grinding instrument has been obtained.

*Constitution of Substances with Co-ordination Number Six.*

The two substances to be considered are sodium chlorate and its analogue sodium bromate, which must naturally have a similar constitution. Since the co-ordination number is six, the co-ordination figure is a regular octahedron, at the centre of which is situated the chlorine atom, with its six co-ordination valencies directed towards the six corners. When the six valencies are satisfied by three doubly bound oxygen atoms, the group  $\text{ClO}_3$  becomes enantiomorphous:



The above constitution is analogous to the one suggested by Werner for the complex chromium oxalate group in the optically active potassium chromium oxalate.

*Constitution of the Substances in the State of Solution.*

The question must now be considered whether the substances under discussion retain the same constitution when dissolved or liquefied, or whether a radical change takes place so as to yield a molecule with a different formula. There appears to be only one available source of evidence in this connexion, namely, ionisation phenomena, which, in fact, point to the conclusion that there is no change of constitution when the substances are dissolved. Sodium chlorate, for example, undergoes electrolytic dissociation into  $\text{ClO}_3$  and  $\text{Na}$  ions, that is, into the co-ordinated and the unco-ordinated parts of the molecules. Again, a solution of magnesium sulphate contains  $\text{Mg}$  and  $\text{SO}_4$  ions, and since the prevailing tendency of opinion is to assume that each ion is surrounded by an envelope of several water molecules, the single water molecule which was received into the co-ordination sphere may perhaps be looked upon

as constituting one of the relatively large number which surround the  $\text{SO}_4$  ion in solution.

If the constitution remains unaltered during the passage of the substance into solution, some explanation must be forthcoming of the inactivity of the solution. This inactivity is probably due to autoracemisation. That there is nothing inherently improbable in this view will perhaps be generally admitted if the constitution of the compounds be compared with those of the substances which have been successfully resolved by Werner. The latter are very prone to racemisation, although the bivalent groups attached to the central atom are of a complex character; representative examples of such groups are ethylenediamine, dipyridyl, and  $\text{C}_2\text{O}_4$ . In particular, the optically active antipodes of potassium chromic oxalate,  $\text{K}_2\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$ , are completely racemised in aqueous solution in seventy-five minutes (Werner, *Ber.*, 1912, **45**, 3063). Now racemisation in such a molecule involves either a flipping of the molecule or a loosening of one of the attachments of each of two  $(\text{C}_2\text{O}_4)$  groups, a rotation of each group about the free ends through an angle of  $60^\circ$ , and a subsequent coupling up. If this process is so easy with a group like  $\text{C}_2\text{O}_4$ , how much more readily should it occur with doubly bonded oxygen atoms, especially as it could be brought about by alternate hydroxylation and dehydration. It is conceivable that autoracemisation should be practically instantaneous on dissolving the crystal. Since no previous experiments appear to have been carried out on this subject, it is proposed to investigate the point, although a positive result is perhaps not to be hoped for.

The reverse change, that is, the crystallisation of the inactive supersaturated solution so as to yield either one or the other crystalline antipode, is equally feasible. When the substance crystallises, the solid phase may be either a conglomerate of active crystals or a racemate. In the former case the accidental appearance of a surplus of *d*- over *l*-crystals will be automatically accompanied by a racemisation of *l*- into *d*-molecules in solution, so that the solution remains inactive.

#### *The Relationship of Sodium Chlorate and Sodium Nitrate.*

The crystalline forms of these two substances are not isomorphous at the ordinary temperature, but at higher temperatures sodium chlorate crystallises in a second modification, isomorphous with the well-known rhombohedral form of sodium nitrate. It must therefore be concluded that the two substances have a similar constitution, and the question must now be entertained why sodium nitrate is not optically active. The absence of rotatory power in

crystals of sodium nitrate receives a satisfactory explanation if it be assumed to be a racemate, that is, a molecular compound of the two antipodes, which in the free state would be isomorphous with sodium chlorate. Some confirmation of the correctness of this view is derived from the following interesting consideration: If a *d*- and an *l*-molecule of sodium nitrate, having configurations similar to those given for sodium chlorate, be allowed to interpenetrate in the most symmetrical way possible, then the symmetry of the racemic molecule thus obtained is found to be identical in every respect with that of a crystal of sodium nitrate, and, moreover, is in complete harmony with the rhombohedral form.

Again, the dimorphism of sodium chlorate now acquires a new significance. The rhombohedral modification of this salt, being isomorphous with the racemic nitrate, must itself also be a racemic compound; and the "dimorphism" of sodium chlorate becomes precisely analogous to that of sodium ammonium tartrate, that is, there is a transition temperature above and below which the racemate and the conglomerate of optical antipodes are the stable phases respectively. The crystalline form, composition, and physical properties of mixed crystals of sodium chlorate and nitrate are also in full accord with the present interpretation. Mallard (*Bull. Soc. franç. Min.*, 1884, 7, 352) has found that at the ordinary temperature the rhombohedral sodium nitrate will take up as much as 22.5 per cent. of sodium chlorate; the optically active, cubic sodium chlorate, however, does not appreciably dissolve the nitrate.

In conclusion, we wish to express our grateful thanks to Prof. H. Hilton for much valuable advice on the theory of crystal structure.

CHEMICAL AND MINERALOGICAL DEPARTMENTS,  
UNIVERSITY MUSEUM, OXFORD.

## LXXXVI.—*The Preparation of Pure Bromine.*

By ALEXANDER SCOTT.

EVERYONE interested in atomic weight work realises the fundamental importance of the reaction between silver and bromides on which so much of the work of Stas and others depends. Any improvement in the preparation either of pure silver or pure bromine therefore requires no apology.

The method for the preparation of pure bromine described by Stas in 1876 (*Mém. Acad. Sci. Bruxelles*, 1881, 42, 90) cannot be

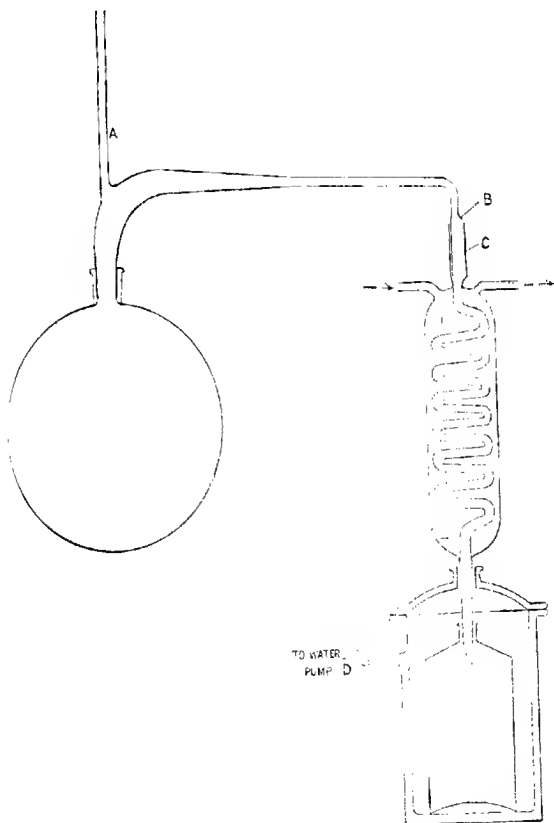
regarded as altogether satisfactory. He distills his bromine from a strong solution of potassium bromide containing in suspension zinc oxide prepared by ignition of the nitrate. This, he says, removes any iodine as iodate, and, of course, any chlorine decomposes an equivalent amount of potassium bromide. Now, however carefully the zinc oxide is prepared in this way, it is almost certain to contain sufficient nitrogen oxides to contaminate the bromine with traces at least of nitric acid. Further, all the organic chlorides and bromides which were originally in the bromine are left in the product so purified. For the great majority of purposes they fortunately do not much matter.

Having to prepare a large quantity of bromine which must be free from organic compounds as well as the other halogens, it occurred to me to prepare it from potassium bromide which had been completely freed from iodine either as iodide or iodate. This was done by boiling a solution of 1500 grams of the bromide in an equal weight of water first with a few crystals of potassium metabisulphite and about 5 c.c. of concentrated sulphuric acid, then adding 100 c.c. of saturated bromine water, distilling off the excess of bromine, adding another 100 c.c. of bromine water, distilling off once more, and, after neutralisation with potassium carbonate, evaporating to dryness. The dried bromide was now fused with potassium dichromate (which had previously been fused) in the proportion of 500 grams of bromide to 200 grams of dichromate. This leaves an excess of bromide sufficient to retain any quantity of chlorine likely to be present. 1050 Grams of the fused mass broken up into pieces the size of hazel nuts were now treated with a *cold* mixture of 450 c.c. of concentrated sulphuric acid with 700 c.c. of water. Any organic matter in this mixture was destroyed by adding a small quantity of potassium permanganate. The above quantities give about 470 grams of bromine, and on the addition of an excess of dichromate a further 30 grams of bromine are obtained, which ought to contain all the chlorine.

Altogether, I prepared about 3250 grams of the pure bromine, together with an additional 183 grams possibly containing chlorine. The purity of the bromine was indicated clearly by the fact that these 183 grams only contained 4 to 5 *milligrams* of chlorine. The 3250 grams were, however, dissolved in potassium bromide solution (which had been freed from iodine as above described), and distilled from it so that I believe I have now got bromine pure enough for my work.

The apparatus employed for the distillations above described is very simple, and the diagram practically explains itself. The chief points to be attended to are that the tube *A* should be about

150 mm. long, and of just sufficient diameter to take a thermometer which can be replaced by a tube for bubbling air through the liquid or simply by a glass rod. The first drops of liquid seal in the air between the lower end of *A* and the small piece of india-

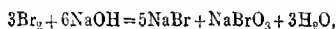


rubber tubing which keeps the thermometer, etc., in position. The tube *B* also should just fit loosely into the condenser tube *C*, and in distilling bromine a drop of water is a sufficient seal between *B* and the condenser. The bottle acting as a receiver is placed in a

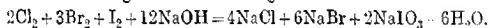
Witt's filtering apparatus with the funnel removed, and *D* connected with a water-pump drawing in a gentle current of air. By means of this apparatus any quantity of bromine may be distilled without its odour causing the slightest inconvenience.

In endeavouring to determine the quantity of iodine which could be detected, and, if possible, its amount determined, I was led to try the effect of sodium hydroxide instead of zinc oxide as a means of removing it from the bromine. Bromates of the alkali metals are so readily decomposed by iodine, even without the addition of any acid, that I thought this might act satisfactorily. Not only so, but the bromide formed simultaneously should also retain the chlorine.

The result of the experiment was successful far beyond my anticipations, and instead of the reaction, which is usually written:



we have something like the following:



To begin with, I added to 10 c.c. of bromine 3 milligrams of iodine (that is, 1 part in 10,000) and then 4 or 5 c.c. of water, along with 1 c.c. of *N*-sodium hydroxide solution. This was shaken vigorously several times, and then the bromine separated from the aqueous liquid, which was heated on the water-bath until colourless, then treated with a slight excess of sulphurous acid; after this excess had been boiled off and the liquid cooled, it was tested with sulphuric acid containing a little nitrite and chloroform, when a very strong iodine reaction was obtained. With 10 c.c. of bromine it is easy to detect the presence of 1 part of iodine in 100,000 of bromine.

Similarly, a known weight of chlorine was passed into 10 c.c. of bromine, and was found to be similarly removed.

Neither chlorine nor iodine could be detected in the residual bromine respectively.

I hope shortly to describe in detail a method for determining the amounts of chlorine and of iodine in bromine, even when present in very small quantity, but as at present employed it is capable of simplification in one or two respects. I shall content myself with practical proofs that bromine shaken up once with a sufficiency of sodium hydroxide solution to combine with the chlorine and iodine present, is to all intents and purposes freed completely from these elements. No doubt for atomic-weight work it would be safer to treat commercial bromine, say, three times, distilling it from a small quantity of very dilute soda finally.

A few examples taken from my notebook will indicate the

quality of the bromine thus produced. The equivalents found with the solutions employed are all rather high. This is due to a small quantity of the halogen being driven off during fusion, and consequently the presence of a small quantity of hydroxide or carbonate, which, of course, raises the equivalent.

The purest bromine prepared as above described was shaken with 5 c.c. of *N*-sodium hydroxide, the aqueous solution evaporated to dryness, and the residue fused so as to decompose the bromate. This residue weighed 0.4737 gram, requiring 45.7 c.c. of *N*/10-silver nitrate:

$$\text{Equivalent} = 103.65;$$

between 0.120 and 0.130 gram of chlorine was passed into 5 c.c. of bromine, and then the bromine shaken with 10 c.c. of *N*-sodium hydroxide, and treated as above, when the residue, weighing 0.8345 gram, required 94.45 c.c.:

$$\text{Equivalent} = 88.35,$$

and chlorine = 0.1232 gram.

The bromine remaining was now shaken with 5 c.c. of *N*-sodium hydroxide as above, when the residue weighed 0.5103 gram, requiring 49.15 c.c. of *N*/10-silver nitrate:

$$\text{Equivalent} = 103.8.$$

The residual bromine was again treated with 5 c.c. of *N*-sodium hydroxide and treated as above, when the residue weighed 0.5023 gram, requiring 48.45 c.c., whence the

$$\text{Equivalent} = 103.7.$$

The 183 grams of bromine referred to previously as possibly containing chlorine (p. 818) were similarly treated with 5 c.c. of *N*-sodium hydroxide, when the residue weighed 0.4899 gram and required 47.7 c.c. of *N*/10-silver nitrate, giving an equivalent = 102.7, corresponding with 0.0044 gram of chlorine.

The bromine remaining was again treated, when the residue weighing 0.4991 gram required 48.15 c.c., and gave the equivalent = 103.65.

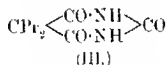
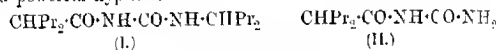
These examples seem to prove conclusively that bromine treated with sodium hydroxide even in such small quantities as above indicated is completely freed from both chlorine and iodine.



# LXXXVII.—*The Application of Hofmann's Reaction to Dialkylacetamides.*

By FRANK LEE PYMAN.

IN the course of work on the relation between chemical constitution and physiological action in hypnotic substances, it was thought desirable to prepare  $\alpha$ -propylbutyryl- $\delta$ -heptylcarbamide (I) for the following reasons. It is known that  $\alpha$ -propylbutyrylcarbamide (II) has hypnotic properties, and so also have various monoalkylcarbamides.  $\alpha$ -Propylbutyryl- $\delta$ -heptylcarbamide might therefore be expected to have the combined hypnotic properties of the two classes of compounds; further, it would be somewhat similarly constituted to dipropylbarbituric acid ("proponal") (III), which is a powerful hypnotic:



The obvious method indicated in the literature for the preparation of  $\alpha$ -propylbutyryl- $\delta$ -heptylcarbamide was Hofmann's reaction, namely, to treat two molecular proportions of  $\alpha$ -propylvaleramide,  $\text{CHPr}_2\cdot\text{CO}\cdot\text{NH}_2$ , with one molecular proportion of bromine and aqueous potassium hydroxide. Experiments showed, however, that this method did not give the desired result, for in the place of the expected compound a mixture of *sed-heptylcarbamide*,  $(\text{CHPr}_2\cdot\text{NH}_2)_2\text{CO}$ , and unchanged  $\alpha$ -propylvaleramide was obtained. This is entirely at variance with the behaviour of the normal aliphatic acid amides in similar circumstances, and gave rise to the investigation herein recorded.

It is now shown that the dialkylacetamides—in particular  $\alpha$ -propylvaleramide, with which the work has chiefly been carried out—do not behave precisely similarly to the normal aliphatic acid amides in respect of their behaviour to bromine and alkali. The differences in behaviour between the acid amides of the two classes may be compared under three headings, namely, (1) formation of the bromoamide, (2) formation of the lower amine, and (3) formation of the acylalkylcarbamide.

## (1) *Formation of the Bromoamide.*

Hofmann (*Ber.*, 1882, **15**, 407, 752) has shown that when a normal aliphatic acid amide is treated with bromine (1 molecule)

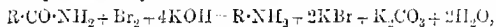
and sodium or potassium hydroxide (1 molecule), the bromoamide is produced as follows:



The bromoamides of acetic and propionic acids were isolated as pure, crystalline compounds, but neither *n*-butyrobromoamide nor any of the higher bromoamides could be isolated in a crystalline condition; *isobutyramide*, however, readily gave a crystalline bromoamide. It has now been found that *α*-ethylbutyrobromoamide and *α*-propylvalerobromoamide can also readily be isolated in crystalline form in almost quantitative yield.

### (2) Formation of the Lower Amine.

Hofmann (*Ber.*, 1882, 15, 762; 1884, 17, 1406, 1920) has shown that the preparation of amines from the normal aliphatic acid amides (1 mol.) by the action of bromine (1 mol.) and excess of aqueous potassium hydroxide:



does not proceed smoothly above the fifth member of the series, and that this is due partly to the formation of nitriles:



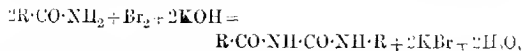
and partly to the formation of the corresponding acylalkylcarbamide.

Thus, *n*-octoamide (which is isomeric with *α*-propylvaleramide) gives only a 30 per cent. yield of *n*-heptylamine.

*α*-Propylvalerobromoamide, however, when treated with an excess of aqueous sodium hydroxide, readily gives an 84 per cent. yield of 5-aminohexane,  $CHPr_2 \cdot NH_2$ ; in this case, of course, no nitrile formation is possible, and as will be shown later there is very little tendency to the formation of the acylalkylcarbamide.

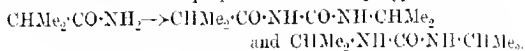
### (3) Formation of the Acylalkylcarbamide.

Hofmann (*Ber.*, 1882, 15, 762) has shown that when the normal aliphatic acid amides (2 mols.) are treated with bromine (1 mol.) and aqueous potassium hydroxide, acylalkylcarbamides are produced in excellent yields throughout the series up to *n*-decanamide, the highest member tested:



and states, for instance, that the yield of heptohexylcarbamide from heptoamide,  $C_6H_{13} \cdot CO \cdot NH_2$ , is nearly quantitative, and that the reaction proceeds with increasing readiness from the eighth member of the series onwards. *n*-Octoamide (the isomeride of

$\alpha$ -propylvaleramide) would, therefore, give an excellent yield of the corresponding acylalkylcarbamide. He tested also three aliphatic acid amides outside the normal series, namely, *isobutyramide*,  $(\text{CHMe}_2\cdot\text{CO}\cdot\text{NH}_2)$ , *isovaleramide*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , and *isohexamide*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ ; the two latter gave normal results, for the corresponding acylalkylcarbamides were obtained, and there is no mention of any by-products. In the case of *isobutyramide*, however, the action of bromine (1 mol.) and aqueous potassium hydroxide on 2 molecules of the acid anide gave rise to a mixture of the acylalkylcarbamide, namely, *isobutyroisopropylcarbamide*, with a small proportion of *s-di-isopropylcarbamide*:



In the long series of acylalkylcarbamides prepared from aliphatic acid amides by Hofmann and subsequent investigators this is the only case in which a by-product of this type has hitherto been observed.

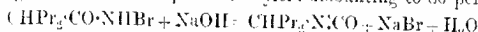
*iso*Butyramide is, of course, the simplest possible dialkylacetamide. Now it has already been stated that the action of bromine (1 mol.) and alkali on  $\alpha$ -propylvaleramide (2 mols.) gave a mixture of *s-di*- $\delta$ -heptylcarbamide and  $\alpha$ -propylvaleramide instead of the acylalkylcarbamide, and it has further been found that  $\alpha$ -methylbutyramide,  $\text{CHMeEt}\cdot\text{CO}\cdot\text{NH}_2$ ,  $\alpha$ -ethylbutyramide,  $\text{CHEt}_2\cdot\text{CO}\cdot\text{NH}_2$ , and  $\alpha$ -ethylvaleramide,  $\text{CHEtPr}\cdot\text{CO}\cdot\text{NH}_2$ , when similarly treated also yield mixtures containing the corresponding *s*-dialkylcarbamides and the unchanged acetamides.

In order to inquire into the cause of the divergence in the behaviour between the normal aliphatic acid amides and the dialkylacetamides, the following experiments were carried out with derivatives of  $\alpha$ -propylvaleramide.

In the first place,  $\alpha$ -propylvalerobromoamide was prepared. This substance appears to have been obtained previously by Fuchs (*Zustsch. angew. Chem.*, 1904, **17**, 1505) for the purpose of a physiological examination, but its chemical and physical properties have not hitherto been described. It was readily obtained in the usual way following the procedure described by Mauguin (*Ann. Chim. Phys.*, 1911, [viii], **22**, 297).  $\alpha$ -Ethylbutyrobromoamide was also prepared in a similar manner. The preparation of  $\alpha$ -propylbutyryl- $\delta$ -heptylcarbamide was then attempted with the pure isolated  $\alpha$ -propylvalerobromoamide in the place of the solution of  $\alpha$ -propylvaleramide in bromine.  $\alpha$ -Propylvalerobromoamide (1 mol.) was mixed with  $\alpha$ -propylvaleramide (1 mol.) and warmed with aqueous sodium hydroxide (1 mol.), when again a mixture of

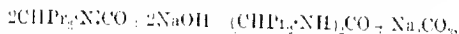
with  $\delta$ -heptylcarbamide with unchanged  $\alpha$ -propylvaleramide was obtained.

In order to determine whether the failure to combine was due to the inertness of the  $\alpha$ -propylvaleramide, a similar experiment was carried out, using acetamide in its place, but here again a mixture containing *s*-di- $\delta$ -heptylcarbamide was obtained. It was thus shown that the nature of the acid amide was not the cause of the failure to form the desired compound. The action of aqueous sodium hydroxide (1 mol.) on  $\alpha$ -propylvalerobromoamide (1 mol.) was then examined; the product when distilled in a current of steam gave  $\delta$ -carbinidoheptane in a yield amounting to 80 per cent.

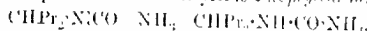


of the theoretical, and a mixture of *s*-di- $\delta$ -heptylcarbamide and  $\alpha$ -propylbutyryl  $\delta$ -heptylcarbamide remained in the residual liquor.

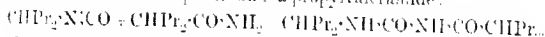
$\delta$ -Carbinidoheptane is only slowly altered by boiling water, for it remained largely unchanged after boiling for one and a-half hours with five times its weight of water. Boiling aqueous sodium hydroxide gradually converts it almost quantitatively into *s*-di- $\delta$ -heptylcarbamide:



and with cold aqueous ammonia it yields  $\delta$ -heptylcarbamide:

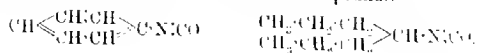


It follows from the experiments previously described that  $\delta$ -carbinidoheptane, even in a nascent condition, does not combine—or at most combines to a very slight extent—with acid amides in the presence of water, but it was found that the required  $\alpha$ -propylbutyryl  $\delta$ -heptylcarbamide could be prepared by directly heating together  $\delta$ -carbinidoheptane and  $\alpha$ -propylvaleramide:

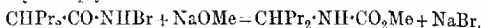


It thus appears that the behaviour of  $\delta$ -carbinidoheptane resembles more closely that of phenylcarbimide than that of the normal aliphatic carbimides, although it is less readily affected by water than phenylcarbimide, which is quickly changed into *s*-di-phenylcarbamide; thus Kühn (*loc. cit.*, 1881, 17, 2880) found that phenylcarbimide when heated with acid amides gave acylphenylcarbamides only in the absence of water, and that in the presence of water diphenylcarbamide was formed.

This similarity of behaviour and divergence from that of the normal aliphatic acid amides may possibly be accounted for by the similarity of steric structure of the two compounds.



In connexion with  $\alpha$ -propylvalerobromoamide, the following point may be mentioned. Jeffreys (*Amer. Chem. J.*, 1899, **22**, 141) has shown that normal aliphatic bromoamides react with sodium methoxide, and less readily with sodium ethoxide, to yield esters of the corresponding alkylcarbamates.  $\alpha$ -Propylvalerobromoamide behaves similarly in this respect, giving excellent yields of methyl and ethyl  $\delta$ -heptylcarbamates in the two cases:



The results of the physiological examination of  $\alpha$ -propylbutyryl- $\delta$ -heptylcarbamide and methyl  $\delta$ -heptylcarbamate were disappointing, neither compound having any marked hypnotic action.

#### EXPERIMENTAL.

##### *Action of Sodium Hydroxide on $\alpha$ -Propylvaleramide (2 mols.) and Bromine (1 mol.).*

7.1 Grams of  $\alpha$ -propylvaleramide were mixed with 4 grams of bromine, and 20 c.c. of 10 per cent. aqueous sodium hydroxide were added, the mixture being cooled in water. After heating on the water-bath, the oil floating on the surface of the aqueous layer became reddish-brown. A further quantity of 10 c.c. of 10 per cent. aqueous sodium hydroxide was then added, and the mixture heated for another half-an-hour, when the oil became almost colourless. The mixture was then cooled, and the solidified oil collected and washed with water, when it amounted to 5.9 grams, melting at 88–90°. On crystallisation from alcohol, 1.5 grams of crude *s*-di- $\delta$ -heptylcarbamide melting at 190–200° first separated, and by recrystallisation of this from the same solvent 1.2 grams of the pure compound were obtained. The mother liquors deposited on dilution with water 3.5 grams of crude  $\alpha$ -propylvaleramide, which melted at 117°, the mixture with the pure amide (m. p. 124°) melting at 119°. The ultimate mother liquors when evaporated to dryness left a solid, which after draining on porous porcelain melted at 95–105°.

It is thus clear that very little, if any,  $\alpha$ -propylbutyryl- $\delta$ -heptylcarbamide, which, it is subsequently shown, melts at 89–90°, can have been formed in this reaction.

In a larger experiment carried out with 35 grams of  $\alpha$ -propylvaleramide, 10 grams of the pure *s*-di- $\delta$ -heptylcarbamide were obtained.

*s*-Di- $\delta$ -heptylcarbamide,  $(\text{CHPr}_2\cdot\text{NH})\text{CO}$ , crystallises from alcohol in colourless needles, which melt at 239–241° (corr.). It is insoluble in boiling water, dilute acid, or alkalis, sparingly soluble in cold alcohol or ether, but readily so in hot alcohol:

0.1192 gave 0.3060  $\text{CO}_2$  and 0.1341  $\text{H}_2\text{O}$ .  $\text{C}=70.0$ ;  $\text{H}=12.6$ .

0.1354 „ 12.9 c.c.  $\text{N}_2$  at  $20^\circ$  and 760 mm.  $\text{N}=11.2$ .

$\text{C}_{12}\text{H}_{22}\text{ON}_2$  requires  $\text{C}=70.3$ ;  $\text{H}=12.6$ ;  $\text{N}=10.9$  per cent.

It dissolves in concentrated sulphuric acid, and is reprecipitated on dilution with water. It is not decomposed by boiling 50 per cent. aqueous potassium hydroxide, but when it is distilled from a metal-bath with fused potassium hydroxide containing a few drops of water,  $\delta$ -aminoheptane passes over between  $240^\circ$  and  $320^\circ$ , accompanied by some unchanged carbamide, and is obtained in a yield amounting to 71 per cent. of the theoretical, allowing for the unchanged material.

The preparation and properties of the following carbamides are similar to the above except that the yields diminish with the size of the molecule.

*Di- $\gamma$ -butylcarbamide*,  $(\text{CH}_2\text{EtPr}\cdot\text{NH})_2\text{CO}$ , which melts at  $220$ – $222^\circ$  (corr.):

0.1500 gave 0.3760  $\text{CO}_2$  and 0.1647  $\text{H}_2\text{O}$ .  $\text{C}=68.4$ ;  $\text{H}=12.3$ .

$\text{C}_{13}\text{H}_{25}\text{ON}_2$  requires  $\text{C}=68.4$ ;  $\text{H}=12.4$  per cent.

*Di- $\gamma$ -amylcarbamide*,  $(\text{CH}_2\text{Et}_2\text{NH})_2\text{CO}$ , which melts at  $212$ – $214^\circ$  (corr.):

0.1200 gave 11.6 c.c.  $\text{N}_2$  at  $23^\circ$  and 770 mm.  $\text{N}=14.3$ .

$\text{C}_{11}\text{H}_{21}\text{ON}_2$  requires  $\text{N}=14.0$  per cent.

*Di- $\beta$ -butylcarbamide*,  $(\text{CHMeEt}\cdot\text{NH})_2\text{CO}$ , which melted at  $131$ – $135^\circ$  (corr.). (Found.  $\text{C}=63.1$ ;  $\text{H}=11.4$ ;  $\text{N}=16.0$ . Calc.,  $\text{C}=62.8$ ;  $\text{H}=11.6$ ;  $\text{N}=16.3$  per cent.) This substance has previously been described by A. E. Dixon (T., 1895, 67, 651), who gives its melting point as  $137$ – $138^\circ$ .

#### *$\alpha$ -Propylvalerobromoamide*, $\text{CHPr}_2\cdot\text{CO}\cdot\text{NHBr}$ .

This substance was prepared by a method similar to that employed by Manguin (*Ann. Chim. Phys.*, 1911, [viii], 22, 297) for the preparation of isobutyrobromoamide.

11.4 Grams of  $\alpha$ -propylvaleramide were dissolved in 40 c.c. of chloroform, and 12.8 grams of bromine added. The solution was then cooled to  $-10^\circ$ , and a solution of 4.5 grams of potassium hydroxide in 160 c.c. of water added gradually with thorough stirring, keeping the temperature below  $0^\circ$ . The product, consisting mainly of ice, was then warmed to  $5^\circ$ , and the separated solid collected, washed with a little water, and drained on porous porcelain. It represented nearly pure bromoamide, amounting usually to from 14 to 15 grams, that is, 79 to 84 per cent. of the theoretical, and melted at  $109^\circ$  or a degree or so higher. For analysis it was recrystallised from diethyl ether, when the pure bromoamide then

separated in colourless, prismatic needles, which melted at  $116^{\circ}$  (corr.) to a red liquid:

0.1328 gave 0.2108  $\text{CO}_2$  and 0.0888  $\text{H}_2\text{O}$ .  $\text{C}=43.3$ ;  $\text{H}=7.5$ ,

0.1658 .. 0.1390  $\text{AgBr}$ .  $\text{Br}=35.7$ .

$\text{C}_8\text{H}_{16}\text{ONBr}$  requires  $\text{C}=43.2$ ;  $\text{H}=7.3$ ;  $\text{Br}=36.0$  per cent.

$\alpha$ -Propylvalerobromoamide is insoluble in cold water, readily soluble in alcohol, moderately so in warm, but sparingly so in cold ether. It decomposes and turns yellow after keeping for a few days.

In the experiments described below, the crude  $\alpha$ -propylvalerobromoamide melting at  $109^{\circ}$  or a little higher was employed.

*$\alpha$ -Ethylbutyrobromoamide,  $\text{C}_4\text{H}_9\text{Br}\cdot\text{CO}\cdot\text{NHBr}$ .*

This substance was prepared in the same way as  $\alpha$ -propylvalerobromoamide, except that it did not crystallise from the product but remained dissolved in the chloroform. After separating this solvent from the aqueous solution and allowing it to evaporate spontaneously,  $\alpha$ -ethylbutyrobromoamide remained. It was purified by crystallisation from dry ether, from which it separates in flat, colourless needles, melting at  $86-87^{\circ}$  (corr.). It is insoluble in water, readily soluble in alcohol, moderately so in warm, but sparingly so in cold ether:

0.1410 gave 0.1929  $\text{CO}_2$  and 0.0752  $\text{H}_2\text{O}$ .  $\text{C}=37.1$ ;  $\text{H}=6.0$ .

0.1570 .. 0.1332  $\text{AgBr}$ .  $\text{Br}=41.2$ .

$\text{C}_6\text{H}_{12}\text{ONBr}$  requires  $\text{C}=37.1$ ;  $\text{H}=6.2$ ;  $\text{Br}=41.2$  per cent.

It gives an excellent yield of  $\gamma$ -aminopentane when distilled with an excess of 10 per cent. aqueous sodium hydroxide.

*$\alpha$ -Propylvalerobromoamide (1 mol.),  $\alpha$ -Propylvaleramide (1 mol.), and Sodium Hydroxide (1 mol.).*

2.2 Grams of  $\alpha$ -propylvalerobromoamide, 1.4 grams of  $\alpha$ -propylvaleramide, and 1 c.c. of 10 per cent. aqueous sodium hydroxide were shaken together when the mixture became warm. It was heated for an hour on the water-bath and then cooled. The separated solid was collected and washed with water, when it amounted to 2.6 grams melting at about  $88-90^{\circ}$ . After fractional crystallisation from alcohol, 0.75 gram of *s*-di- $\delta$ -heptylcarbamide (m. p.  $235^{\circ}$ ) and 1.1 grams of  $\alpha$ -propylvaleramide (m. p.  $122^{\circ}$ ) were isolated from the mixture.

Little, if any, combination between the  $\delta$ -carbimidoheptane, which would be formed by the action of the alkali on the bromoamide, and the  $\alpha$ -propylvaleramide can therefore have taken place.

A similar result was arrived at in the case of  $\alpha$ -ethylbutyrobromoamide and  $\alpha$ -ethylbutyramide.

*$\alpha$ -Propylvalerobromoamide (1 mol.), Acetamide (1 mol.), and Sodium Hydroxide (1 mol.).*

2.2 Grams of  $\alpha$ -propylvalerobromoamide, 0.6 gram of acetamide, and 4 c.c. of 10 per cent. aqueous sodium hydroxide were mixed, digested for one hour on the water-bath, and distilled in a current of steam. Only traces of oil passed over with the steam, and the residue, which was obviously a mixture, readily gave on crystallisation from alcohol a quantity of *s*-diheptylcarbamide. After 0.3 gram of this compound had been isolated in a pure state the separation was not carried out further.

*$\alpha$ -Propylvalerobromoamide and Excess of Sodium Hydroxide. Formation of  $\delta$ -Aminoheptane.*

11.1 Grams of  $\alpha$ -propylvalerobromoamide were shaken with 111 c.c. of 10 per cent. aqueous sodium hydroxide. After keeping for ten minutes the solution was distilled in a current of steam, when the amine passed over as an oil, which was sparingly soluble in water. The distillation was continued so long as an alkaline distillate was obtained. The latter was then slightly acidified with hydrochloric acid and evaporated to dryness, when 6.4 grams of  $\delta$ -aminoheptane hydrochloride melting at  $240^\circ$  were obtained, that is, 81 per cent. of the theoretical. After crystallisation from water this salt formed needles, which melted at  $246\text{--}247^\circ$  (corr.). It is readily soluble in cold water, and very readily so in hot water or absolute alcohol. (Found, C = 54.9; H = 11.7; Cl = 23.3. Calc., C = 55.4; H = 11.3; Cl = 23.1 per cent.) Noyes (*Amer. Chem. J.*, 1893, **15**, 542), who has previously prepared  $\delta$ -aminoheptane by the reduction of dipropylketoxime, gives the melting point of this salt as  $241\text{--}242^\circ$ .

$\delta$ -Aminoheptane hydrochloride crystallises from water in plates, which decompose at about  $235^\circ$  (corr.). It is readily soluble in hot, but rather sparingly so in cold water:

0.3158 (dried at  $100^\circ$ ) gave 0.0955 Pt. Pt = 30.2

( $C_7H_{17}N$ )<sub>20</sub>.PtCl<sub>6</sub> requires Pt = 30.4 per cent.

*$\alpha$ -Propylvalerobromoamide (1 mol.) and Sodium Hydroxide (1 mol.). Formation of  $\delta$ -Carbimidoheptane,  $CHPr_2NCO$ .*

11.1 Grams of  $\alpha$ -propylvalerobromoamide were shaken with a solution of 2 grams of sodium hydroxide in 20 c.c. of water. The mixture became warm, and the solid was converted into an oil,



On distillation in a current of steam the product was separated into two fractions.

*δ*-Carbimidoheptane passed over with the steam, and after separation from the water amounted to 5.6 grams, that is, 80 per cent. of the theoretical yield. After distillation under normal pressure it passed over almost completely at 171° (corr.) as a colourless oil:

0.1590 gave 0.3958 CO<sub>2</sub> and 0.1564 H<sub>2</sub>O. C=67.9; H=11.0.

C<sub>8</sub>H<sub>15</sub>ON requires C=68.1; H=10.7 per cent.

The residual liquor after the steam distillation contained an oil which solidified on cooling. This amounted to 1.5 grams, and melted at about 95–100° after sintering earlier. Treatment with ether separated it into *s*-di-*δ*-heptylcarbamide, which is sparingly soluble in this solvent, and *α*-propylbutyryl-*δ*-heptylcarbamide, which is readily soluble.

*Action of Boiling Water and Sodium Hydroxide on δ*-Carbimidoheptane.—Two grams of *δ*-carbimidoheptane were boiled with 10 c.c. of water for one and a-half hours under a reflux condenser; on cooling, the oil remained largely unchanged, still having the characteristic odour and power of irritating the eyes possessed by carbimides; it contained, however, a small amount of silky needles, probably *s*-di-*δ*-heptylcarbamide. Five c.c. of water containing 1.5 grams of sodium hydroxide were then added, and the mixture again boiled for one and a-half hours. The resulting solid was then collected, washed with water, and dried at 100°, when 1.6 grams of pure *s*-di-*δ*-heptylcarbamide melting at 237° were obtained; that is, 89 per cent. of the theoretical.

*Action of Ammonia on δ*-Carbimidoheptane.—When *δ*-carbimidoheptane is shaken with 10 per cent. aqueous ammonia it is gradually converted into *δ*-heptylcarbamide, CHPr<sub>2</sub>·NH·CO·NH<sub>2</sub>, which crystallises from alcohol in colourless needles, melting at 173° (corr.):

0.0820 gave 12.1 c.c. N<sub>2</sub> at 16° and 750 mm. N=17.3.

C<sub>8</sub>H<sub>17</sub>ON<sub>2</sub> requires N=17.7 per cent.

*α*-Propylbutyryl-*δ*-heptylcarbamide. CHPr<sub>2</sub>·CO·NH·CO·NH·CHPr<sub>2</sub>.

0.5 Gram of *δ*-carbimidoheptane and 0.5 gram of *α*-propylvaleramide were gradually heated together over a small flame under reflux to 200°; the liquid was then allowed to cool and recrystallised from alcohol, when 0.5 gram of the mixed carbamide melting at 89–96° was obtained in small prisms:

0.1240 gave 0.3066 CO<sub>2</sub> and 0.1276 H<sub>2</sub>O. C=67.4; H=11.5.

0.1160 .. 10.2 c.c. N<sub>2</sub> at 22° and 744 mm. N=10.0.

C<sub>12</sub>H<sub>23</sub>O<sub>2</sub>N<sub>2</sub> requires C=67.5; H=11.3; N=9.9 per cent.

It is insoluble in water, readily soluble in cold alcohol, and very readily so in ether or hot alcohol.

*$\alpha$ -Propylvalerobromoamide (1 mol.) and Sodium Methoxide (1 mol.).*  
*Formation of Methyl  $\delta$ -Heptylcarbamate,  $\text{CHPr}_2\cdot\text{NH}\cdot\text{CO}_2\text{Me}$ .*

3.3 Grams of  $\alpha$ -propylvalerobromoamide were suspended in 10 c.c. of methyl alcohol, and a solution of 0.35 gram of sodium in 5 c.c. of methyl alcohol was added at once at the room temperature. The liquor at once became clear, then hot, and began to boil. After boiling for another half-an-hour under reflux, the methyl alcohol was distilled off, and the residue diluted with water. This caused the separation of *methyl  $\delta$ -heptylcarbamate* as an oil, which quickly became crystalline and then melted at  $42^\circ$ . This product distilled completely at  $223^\circ$  under normal pressure, and solidified on cooling, forming needles, which melted at  $45\text{--}46^\circ$  (corr.). 2.0 Grams of the distilled product were obtained, that is, 79 per cent. of the theoretical:

0.1240 gave 0.2832  $\text{CO}_2$  and 0.1234  $\text{H}_2\text{O}$ .  $\text{C}=62.3$ ;  $\text{H}=11.1$ .

$\text{C}_9\text{H}_{19}\text{O}_2\text{N}$  requires  $\text{C}=62.4$ ;  $\text{H}=11.0$  per cent.

It is insoluble in water, but very readily soluble in alcohol or ether.

*Ethyl  $\delta$ -heptylcarbamate,  $\text{CHPr}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$* , was similarly prepared in 80 per cent. yield, using sodium ethoxide in ethyl-alcoholic solution. It distils at  $230\text{--}231^\circ$  under normal pressure, and melts at  $29\text{--}30^\circ$  (corr.):

0.1358 gave 0.3218  $\text{CO}_2$  and 0.1366  $\text{H}_2\text{O}$ .  $\text{C}=64.6$ ;  $\text{H}=11.3$ .

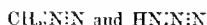
$\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}$  requires  $\text{C}=64.1$ ;  $\text{H}=11.3$  per cent.

WELLCOME CHEMICAL WORKS,  
 DARTFORD, KENT.

# LXXXVIII. — *Constitution of Aliphatic Diazo-compounds.*

By MARTIN ONSLOW FORSTER and DAVID CARDWELL.

NEARLY two years have elapsed since Thiele (*Ber.*, 1911, **44**, 2522) advocated a suggestion thrown out from time to time by others, to the effect that diazomethane and hydrazoic acid should be regarded as having the structure:



respectively, instead of the cycloid types hitherto accepted. Fresh

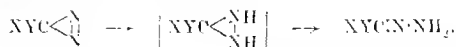
evidence in favour of these formulæ was not put forward at the time, nor has it appeared since, and as this claim has been obediently admitted by other workers, there is no little danger that an idea fundamentally altering our conception of quinquivalent nitrogen should be allowed, prematurely, to be embraced as a fact.

The question of the azoimide nucleus was discussed by one of us in a paper presented to the VIIIth International Congress of Applied Chemistry, and it is therefore unnecessary to deal with this branch of the problem in the present communication. It is worth while to point out, however, that the cardinal objection to Thiele's formula for azoimides remains unanswered. Whilst it is true that certain compounds may be represented by formulæ in which quinquivalent nitrogen is non-ionisable, such as dimethyl-aniline oxide,  $C_6H_5N(CH_3)_2O$ , and *N*-alkyl oxime ethers,  $X\cdot CH\cdot NXYO$ , certainly no case is known in which quinquivalent nitrogen is satisfied by the equivalent of a single element or of groups having the same polarity. A formula which does violence to existing conceptions of this important element must first be based on the clearest possible evidence.

The claim to represent aliphatic diazo compounds in the manner indicated is associated with the structure of condensation products from hydrazine and carbonyl derivatives, which must now be definitely accepted as that of hydrazones,  $XYC\cdot N\cdot NH_2$ , rather than hydrazo-compounds,  $XYC\begin{smallmatrix} \diagup N \\ \diagdown H \end{smallmatrix}$  (Forster and Zimmerli, T., 1910, **97**, 2156; Staudinger and Kupfer, *Ber.*, 1911, **44**, 2197; Thiele, *loc. cit.*; and Wolff, *Abhandl.*, 1912, **394**, 23). Thiele argues that the facility of conversion between hydrazones and diazo-compounds:



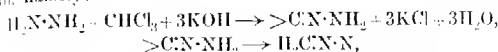
favours his formula and excludes the cycloid. He ignores the possible operation of the Hofmann-Curtius reaction, which, as already indicated (T., 1910, **97**, 2162) supplies an adequate explanation. The suggestion that chemical reaction should attack always the azo-group does not appear very cogent, because although reduction probably does attack it, forming a cycloid so unstable that it passes forthwith to the hydrazone:



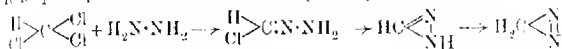
the great activity of aliphatic diazo compounds in other respects may be explained by the tendency of a three-atom ring to undergo disruption under chemical influence.

The contribution to this question by Staudinger and Kupfer (*Ber.*, 1912, **45**, 200), although bringing to light a simple and con-

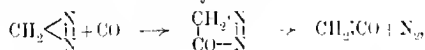
venient method of preparing diazomethane, is not convincing from a theoretical point of view. Instead of the course represented by them, namely:



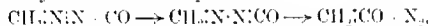
it is quite probable that the following changes take place:



The production of keten from diazomethane and carbon monoxide might arise from an unstable cycloid:



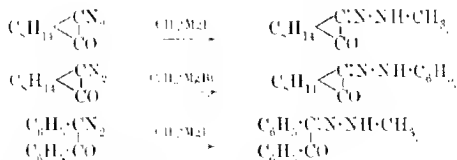
instead of by the alternative process:



the former series being in agreement with several changes of diazomethane too well known to be quoted again.

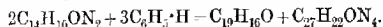
The more recent investigations of Darapsky and Prabhakar (*Ber.*, 1912, **45**, 1654, 2617) into the reduction of diazoacetic ester, although confirming the hydrazone structure for the initial product of this action, do not elucidate the constitution of the original material; moreover, it is noteworthy that Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3022), examining the absorption spectra of typical diazo-compounds, have found no justification for replacing the cycloid by Thiele's formula.

From the foregoing remarks it should be clear that more evidence must be produced before a final conclusion on this question can be drawn. We have therefore studied the effect of the Grignard reaction on diazoamphor and on diazodeoxybenzoin, those two compounds being selected as likely to yield readily identified products. Magnesium methyl iodide and magnesium phenyl bromide were used, and three of the four changes proceeded quite smoothly, yielding the corresponding substituted hydrazone of the original diketone:



The action of magnesium phenyl bromide on diazodeoxybenzoin, although, as will be seen later, pointing in the same direction, is much more complicated, involving these materials in the molecule

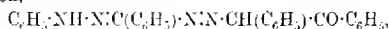
proportion of 3:2, and accompanied by elimination of benzo-phenone, which appears in the form of triphenylcarbinol:



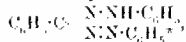
The nitrogenous product,  $\text{C}_{27}\text{H}_{22}\text{ON}_4$ , is a very remarkable compound, crystallising in silky, deep-red needles, and forming intensely coloured solutions in organic media, with which it shows a tendency to unite. Hydrogen chloride combines with it in a single molecular proportion, forming a pale buff hydrochloride, which is slowly dissociated by a large quantity of cold water. Acetic anhydride forms the usual deep red solution, which gradually fades, owing to production of a pale yellow monoacetyl derivative, which is rapidly hydrolysed by alcoholic alkali regenerating the original material. Although an acetone solution of potassium permanganate is decolorised immediately, the product could not be identified, but the action of ferric chloride is very definite, leading to 1:4-diphenyl-1:2:3:5-tetrazole (Wedekind, *Ber.*, 1896, **29**, 1854; Dimroth, *Ber.*, 1907, **40**, 2402), in association with benzoic acid; as the tetrazole contains only one phenyl group attached to nitrogen, the other being combined with an atom of carbon, it would appear that unless the Grignard agent has added phenyl to carbon, it has not added more than one such group to the original molecule, which must therefore contain the residue of both diazodeoxybenzoin molecules involved in the above equation. That it contains a benzoyl group is indicated by the fact that ethyl benzoate is produced when the alcoholic solution is boiled with hydrochloric acid, as also by the circumstance that benzoic acid accompanies the diphenyltetrazole in the ferric chloride oxidation.

Whilst the action of acetic anhydride indicates the presence of hydroxylic oxygen, it was not overlooked that this might arise from a process of enolisation brought about by the agent, and it was therefore necessary to ascertain whether the red substance is ketonic. The action of hydroxylamine acetate, however, which was studied from this point of view, unexpectedly gave rise to 2:5-diphenyl-1:3:4-triazole (Pinner, *Annalen*, 1897, **297**, 255), indicating a very profound disruption of the molecule.

Taking all the circumstances into consideration, we suggest that the red substance produced by the action of magnesium phenyl bromide on diazodeoxybenzoin is a formazyl derivative of the constitution,

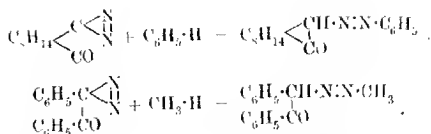


a substance derived from formazylbenzene,

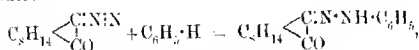


by replacing the asterisked phenyl group with a deoxybenzoin



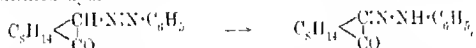


The alternative constitution should lead to substituted hydrazones:



the course actually followed by the experiments.

We believe that this is the best evidence yet furnished for Thiele's formula, but there is one objection to it, namely, the uncertainty whether the azo-compound which should be produced from the cycloid diazo-derivative is capable of separate existence. It seems quite probable that such a substance would change to the isomeric substituted hydrazone:



because the latter substance is produced instead of the former when a diazonium salt acts on the sodium salt of camphorcarboxylic acid or hydroxymethylenecamphor; on the other hand, there has been described a benzeneazidoxybenzoin distinct from benzilphenylhydrazone, so that in this case at least there should be no reason for the azo-compound to change into the phenylhydrazone, but then this is the very case which is complicated by the production of the formazyl derivative.

In conclusion, it should be mentioned that the methylhydrazone of camphorquinone has been obtained in two stereoisomeric forms, the colourless  $\alpha$ -derivative melting at 133°-131° and having  $[\alpha]_D^{25}$  367.5°, and the yellow  $\beta$ -derivative, which melts at 16°, has  $[\alpha]_D^{25}$  296°, and changes into the stable modification when heated. These two forms of camphorquinonemethylhydrazone are strictly comparable with the pairs of hydrazones, semicarbazones, and phenylhydrazones of camphorquinone already described (Forster and Zimmerli, T., 1910, **97**, 2156; 1911, **99**, 478).

## EXPERIMENTAL.

### *Action of Grignard Agents on Diazocamphor.*

Three grams of diazocamphor dissolved in 25 c.c. of dry ether was gradually added to the cooled Grignard agent prepared from 5 grams of methyl iodide and 0.8 gram of magnesium in 50 c.c. of dry ether; the additive product separated as a greyish, semi-solid

mass without liberation of nitrogen, and was decomposed with ice and ammonium chloride. On evaporating the ether by a current of air, colourless needles remained embedded in a small proportion of oil, the latter being removed by cold petroleum; the solid product was readily soluble in benzene, from which it was precipitated by petroleum in needles melting at 133–134°, identical with camphorquinone- $\alpha$ -methylhydrazone (see below):

0.0980 gave 13.1 c.c.  $N_2$  at 24° and 766 mm.  $N = 15.0$ .

$C_{11}H_{15}ON_2$  requires  $N = 11.4$  per cent.

*Camphorquinone- $\alpha$ -methylhydrazone*,  $C_{11}H_{15}N_2$ , was

prepared by shaking during four hours, 6 grams of camphorquinone in 10 c.c. of alcohol with 16 grams of methylhydrazine sulphate and the quantity of concentrated aqueous sodium hydroxide necessary to liberate the base; after remaining twelve hours at 40°, the liquid was diluted with water, which precipitated the methylhydrazone, freely soluble in cold organic media excepting petroleum. A solution containing 0.2600 gram in chloroform diluted to 25 c.c. gave  $\alpha_D$  11°28' in a 3-dm. tube, whence  $[\alpha]_D$  367.5°, falling to 265.0° in the course of five weeks.

*Camphorquinone- $\beta$ -methylhydrazone* arose from the colourless modification on passing a current of steam through a suspension in 10 per cent. aqueous potassium hydroxide, being extracted from the distillate by ether; when this was dried and evaporated, some unchanged  $\alpha$  modification was deposited, but extraction with cold petroleum (b. p. 40–50°) removed the new isomeride, which is freely soluble, separating on spontaneous evaporation in hard, transparent, pale yellow crystals, melting at 46°.

0.1232 gave 15.0 c.c.  $N_2$  at 20° and 756 mm.  $N = 14.2$ .

$C_{11}H_{15}ON_2$  requires  $N = 14.4$  per cent.

A solution containing 0.2779 gram in chloroform diluted to 25 c.c. gave  $\alpha_D$  9°52' in a 3-dm. tube, whence  $[\alpha]_D$  295.9°, falling to 262.1° in the course of four months.

This modification must be regarded as the unstable form, because it changes slowly into the less fusible isomeride when preserved in the sulphuric acid desiccator, although resisting this alteration when calcium chloride alone is present; moreover, when hydrogen chloride is passed into an ethereal solution, the colourless hydrochloride which is precipitated yields the  $\alpha$ -methylhydrazone when treated with sodium carbonate. Thus the physical characteristics of the two methylhydrazones are in precise agreement with the respective members of the series already described (*loc. cit.*).

When diazoamphor was treated with magnesium phenyl bromide,



the additive compound again separated without liberation of gas, and on decomposition with water yielded camphorquinone  $\alpha$ -phenylhydrazone.

*Action of Magnesium Methyl Iodide on Diazodeoxybenzoin.*

Diazodeoxybenzoin is best prepared from benzilhydrazone by agitating a suspension in dry ether with yellow mercuric oxide, the readiness with which the solvent evaporates leading to a more easily purified product than when benzene is employed. Three grams in 25 c.c. of ether was added to the Grignard agent prepared from 5 grams of methyl iodide and 0.8 gram of magnesium in 50 c.c. of ether. The additive compound was brown, and, on proceeding in the usual manner, 2 grams of crystalline material was obtained, precipitated by petroleum from a benzene solution in colourless needles, melting at  $138^{\circ}$ , not depressed by admixture with benzil-methylhydrazone (see below):

0.1546 gave 16.1 c.c. of  $N_2$  at  $20^{\circ}$  and 770 mm.  $N=12.1$ .

$C_{13}H_{14}ON_2$  requires  $N=11.8$  per cent.

*Benzil-methylhydrazone*,  $C_6H_5C(=O)N \cdot NH \cdot CH_3$ , prepared by heating

5 grams of benzil in 10 c.c. of alcohol with 7 grams of methylhydrazine sulphate and 6.5 grams of potassium hydroxide in 20 c.c. of water during six hours under reflux, is readily soluble in organic media excepting petroleum, but is insoluble in water.

*Action of Magnesium Phenyl Bromide on Diazodeoxybenzoin.*

On adding an ethereal solution of the diazo compound (3 grams) to the Grignard agent prepared from bromobenzene (5 grams) and magnesium (0.8 gram), the first few drops developed an intense, purple coloration, changing with more material to a brilliant blue-black, and becoming once more purple at the close of the action. The additive product was brownish-purple, and when decomposed with ice and ammonium chloride, yielded a dark red ethereal solution, leaving the water colourless. On evaporation, the oily residue soon deposited crystals, which were drained from bromobenzene and rubbed with a small quantity of methyl alcohol; this removed triphenylcarbinol, leaving a dark red product, which crystallised from much hot methyl alcohol in cinnabar needles, melting at  $152^{\circ}$ :

0.1375 gave 0.3888  $CO_2$  and 0.0693  $H_2O$ .  $C=77.1$ ;  $H=5.6$ .

0.1196 „ 13.8 c.c.  $N_2$  at  $20^{\circ}$  and 760 mm.  $N=13.5$ .

$C_{27}H_{22}ON_4$  requires  $C=77.5$ ;  $H=5.3$ ;  $N=13.4$  per cent.

The substance displays a tendency to combine with organic

solvents; for instance, in benzene it first dissolves, and then separates in bulky crystals, soluble in a further quantity of the hydrocarbon, forming a daumon-coloured solution, from which petroleum precipitates silky, red needles. It sometimes happens that the deposit from the original ethereal solution is dark brown, and we believe that this is due to bromobenzene of crystallisation, because the brown crystals retained their colour when rubbed with cold methyl alcohol, but formed a dark red solution in much hot methyl alcohol, the cinnabar needles deposited therefrom becoming brown again when treated with hot bromobenzene.

On treating a very dilute solution in cold alcohol with a few drops of aqueous sodium hydroxide, the clear, pale red liquid becomes intensely claret-coloured, but dilution with much water restores the original red colour. The solution in concentrated sulphuric acid is deep red, becoming emerald green with a very small proportion of water, further dilution precipitating a pale brown, amorphous substance which has not been identified. With ammoniacal silver oxide, the alcoholic solution gives a greenish-yellow precipitate, but silver is not deposited even when the solution is boiled; similarly, mercury acetamide is not reduced, but yields a flocculent, yellow precipitate.

*The Hydrochloride.*—When rubbed with cold dilute hydrochloric acid, the red substance became pale yellow, the colour being restored by alcohol or much water. On passing dry hydrogen chloride into an ethereal solution, this rapidly became colourless, depositing a pale buff powder, which began to darken at about  $140^{\circ}$ , and decomposed at the melting point of the original material:

0.1805 gave 0.0562 AgCl. Cl = 7.7.

$C_{27}H_{22}ON_4HCl$  requires Cl = 7.8 per cent.

In absolute alcohol the hydrochloride forms a pale yellow solution, but on adding water the red colour is immediately developed, owing to removal of hydrogen chloride.

*The Acetyl Derivative.*—On dissolving the red substance in hot acetic anhydride, the colour fades rapidly, and the same change occurs more slowly when the solid remains suspended in the agent during four hours at  $40^{\circ}$ ; on shaking the pale yellow solution with water a yellow solid is slowly produced, but although freely soluble in alcohol, benzene, acetone, or ethyl acetate and sparingly soluble in cold petroleum, it could not be crystallised. The amorphous material melted at  $99^{\circ}$ :

0.0526 gave 5.6 c.c.  $N_2$  at  $20^{\circ}$  and 755 mm. N = 12.3.

$C_{27}H_{21}ON_4Ac$  requires N = 12.2 per cent.

$C_{27}H_{20}ON_4Ac_2$  „ N = 11.2 „

VOL. CIII.

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The acetyl derivative resists the action of boiling water, but rapidly develops a red coloration with alcoholic alkali, clearly indicating a hydrolysable acetyl derivative as distinguished from an acetate.

*Action of Ferric Chloride.*—On adding aqueous ferric chloride to an alcoholic solution of the red substance, the colour faded rapidly, ferrous salt being recognisable in the liquid; water precipitated a flocculent material, which was crystallised first from diluted alcohol and finally from petroleum, when it melted at  $101.5-102^{\circ}$ :

0.1243 gave 0.3201  $\text{CO}_2$  and 0.0553  $\text{H}_2\text{O}$ .  $\text{C}=70.2$ ;  $\text{H}=4.9$ .

0.1213 „ 25.8 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 768 mm.  $\text{N}=25.2$ .

$\text{C}_{12}\text{H}_{10}\text{N}_4$  requires  $\text{C}=70.3$ ;  $\text{H}=4.5$ ;  $\text{N}=25.2$  per cent.

This formula and the properties of the compound identify it with 1:4-diphenyl-1:2:3:5-tetrazole, which was obtained by oxidising the tetrazolium chloride derived from *p*-hydroxyformazylbenzene (Wedekind, *loc. cit.*). The aqueous alcoholic filtrate from the precipitated diphenyltetrazole was found to contain benzoic acid, indicating the presence of a benzoyl group in the original compound.

*Action of Hydroxylamine.*—An alcoholic solution of the red substance was heated with aqueous hydroxylamine acetate during four hours under reflux, when the colour faded, and water precipitated a pale brown material; this, when dry, was treated with small quantities of cold benzene, which removed a freely soluble, intensely brown, fluorescent product, which was not identified. The residue dissolved very readily in cold methyl alcohol, separating on addition of water in lustrous needles, which changed to transparent plates; in the desiccator the crystals became opaque, and then melted at  $191^{\circ}$ :

0.1051 gave 0.2927  $\text{CO}_2$  and 0.0490  $\text{H}_2\text{O}$ .  $\text{C}=75.9$ ;  $\text{H}=5.2$ .

0.1117 „ 18.3 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 760 mm.  $\text{N}=19.2$ .

$\text{C}_{12}\text{H}_{11}\text{N}_3$  requires  $\text{C}=76.0$ ;  $\text{H}=5.0$ ;  $\text{N}=19.0$  per cent.

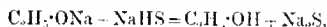
The formula and properties of this product agree with those of 2:5-diphenyl-1:3:4-triazole,  $\text{N} \begin{smallmatrix} \text{CPh} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{Ph} \cdot \text{N} \quad \text{NH} \end{smallmatrix}$ , which was identified further by conversion into the acetyl derivative melting at  $105^{\circ}$ .

# LXXXIX.—*The Conversion of Sodium Hydrosulphide into Sodium Monosulphide.*

By JOHN SMEATH THOMAS and ALEXANDER RULE.

IN a previous paper (T., 1911, **99**, 558) one of us described the action of hydrogen sulphide on the alkyl oxides of sodium and potassium in alcoholic solution. This action affords a simple method of obtaining the pure anhydrous hydrosulphides of those metals.

One of the objects of the present investigation was to ascertain if a reaction analogous to that made use of in the preparation of sodium monosulphide in aqueous solution took place between sodium hydrosulphide and sodium ethoxide according to the equation:



The preparation of the anhydrous monosulphide of sodium in a state of purity appears to be a matter of considerable difficulty. Hugot (*Compt. rend.*, 1899, **129**, 388) describes the preparation by the action of sodium on sulphur in liquid ammonia, the product being a white, amorphous solid. Böttger (*Annalen*, 1884, **223**, 355) and others describe the preparation of the anhydrous monosulphide by dehydrating the hydrated substance in a current of hydrogen. This method has been repeated by the authors of the present paper, and it is found to be quite unsuitable, as the product is always brown, and gives a precipitate of sulphur when treated with hydrochloric acid. In view of our investigations concerning the action of heat on sodium hydrosulphide, the colour of the above product may be explained as due to the partial hydrolysis of the monosulphide by the water derived from the decomposition of the hydrate, and the subsequent dissociation of sodium hydrosulphide produced, with the formation of hydrogen sulphide.

When equimolecular quantities of sodium ethoxide and sodium hydrosulphide are mixed together under varying conditions, it is found that the reaction mentioned above is never complete, sodium ethoxide always being present to some extent in the final product.

By increasing the concentration of one of the components, namely, the ethoxide, it is possible, however, to convert the hydrosulphide completely into the monosulphide.

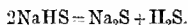
It must therefore be concluded that the reaction:



is reversible, and that sodium monosulphide in alcoholic solution undergoes alcoholysis, analogous to the hydrolysis that takes place in aqueous solution.

Owing to the difficulty of separating the mixture of monosulphide and ethoxide without loss of the former, the reaction does not form a convenient method for the preparation of sodium monosulphide.

The action of heat on the hydrosulphide is interesting, for, starting with the anhydrous hydrosulphide, it should, theoretically, be possible to bring about the dissociation of that compound, thus:



The authors find that this simple change can be effected, but that under ordinary conditions it is complicated by a secondary reaction.

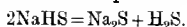
When either sodium or potassium hydrosulphide is heated in the air it becomes yellow below  $100^\circ$ , and as the temperature is raised, the substance darkens in colour, until finally it fuses to a very dark red liquid. On cooling, the order of change of colour is reversed, but the cold solid is always yellow, and always contains polysulphide sulphur. This colour change also takes place when the hydrosulphide is heated rapidly in a vacuum, or in an atmosphere of hydrogen or hydrogen sulphide.

As a result of the experiments described below, the authors attribute the coloration entirely to the action of sulphur produced by the dissociation of hydrogen sulphide, the latter being derived from the dissociation, in the first place, of the hydrosulphide. The hydrosulphides are readily acted on by sulphur with the formation of polysulphides which possess intense colouring power, a mere trace of sulphur being sufficient to bring about a distinct coloration of an alcoholic solution of the hydrosulphide.

Analysis of the mass obtained after rapidly heating the hydrosulphide to fusion and allowing to cool shows that the composition of the substance is not greatly changed, but the small amount of polysulphide which is always present is sufficient to account for the intense yellow colour of the products.

In every case hydrogen sulphide is a product of the action of heat, and can be readily recognised. It is therefore difficult to understand the statement made by Bloxam (T., 1900, **77**, 753) in connexion with potassium hydrosulphide, that the latter compound is stable towards heat, and will bear comparison with its oxygen analogue, potassium hydroxide.

In the case of sodium hydrosulphide our experiments show that the compound exhibits a distinct dissociation pressure at temperatures considerably below its melting point. By heating it in a vacuum with gradual rise of temperature and continuous removal of the hydrogen sulphide evolved, it has been found possible to bring about complete dissociation of the hydrosulphide into the monosulphide in the sense of the equation:



Although under these conditions the dissociation of hydrogen sulphide is increased, the extent of the secondary reaction mentioned above is rendered negligible, as the concentration of the gaseous phase is always exceedingly low.

#### EXPERIMENTAL.

##### *Mixture of Equimolecular Proportions of Sodium Ethoxide and Sodium Hydrosulphide in Alcoholic Solution.*

##### *Solution Allowed to Crystallise in a Vacuum.*

One gram of sodium was dissolved in 20 c.c. of absolute ethyl alcohol, and the solution saturated with hydrogen sulphide. The excess of hydrogen sulphide was removed by warming on the water-bath and passing a rapid current of hydrogen through the solution. The solution of sodium hydrosulphide obtained in this way was treated with a solution of sodium ethoxide prepared by dissolving 1 gram of sodium in 20 c.c. of absolute alcohol. The mixture was kept in a vacuum over calcium chloride, and the crystalline crusts which separated were removed, washed with a little alcohol, and allowed to dry in a vacuum.

The product fused on heating to a dark yellow liquid. Alcohol was evolved, and a strong odour of mercaptan was emitted. On heating more strongly, partial charring took place. The substance behaved as a mixture of the hydrosulphide and the ethoxide, containing a certain amount of alcohol of crystallisation.

This method therefore does not yield the monosulphide, and it was discarded in favour of precipitation with ether, the method used in the preparation of the hydrosulphide (*loc. cit.*).

*Precipitation with Ether.*—The mixture of hydrosulphide and ethoxide was made up as described in the previous experiment. The mixture was boiled for two hours under reflux in a current of hydrogen, allowed to cool, and then poured into much dry ether. A white, crystalline precipitate was produced, which was collected, washed with ethyl alcohol and ether, and dried in a vacuum:

0.2815 gave 0.2560  $\text{Na}_2\text{SO}_4$   $\text{Na} = 29.46$ .

0.1083 „ 0.8525  $\text{BaSO}_4$   $\text{S} = 28.68$ .

The substance contained a considerable proportion of alcohol, which was evolved on heating.

Ratio Na : S in product = 1 : 0.9735.

Ratio Na : S in  $\text{NaHS}$  = 1 : 1.3913.

Ratio Na : S in  $\text{Na}_2\text{S}$  = 1 : 0.6956.

According to these figures, the product consisted of a mixture of hydrosulphide and monosulphide in nearly equimolecular proportions, together with a certain amount of alcohol.

A series of experiments was carried out in which the relative amount of sodium ethoxide to one gram-molecule of hydrosulphide was varied from one to three gram-molecules. Alcohol was removed from the solution by evaporation in a rapid current of hydrogen until solid just began to separate on the sides of the vessel. The solution was then poured into ether, and the product collected, washed with alcohol in order to remove sodium ethoxide as far as possible, then dried in a vacuum and analysed. The figures indicated that the proportion of sodium monosulphide gradually increased until when three gram-molecules of ethoxide were present a product was obtained which gave the following results on analysis:

0.3646 gave 0.1183  $\text{Na}_2\text{SO}_4$ , Na = 37.16.

0.3444 „ 0.6412  $\text{BaSO}_4$ , S = 25.56.

Alcohol (diff.) = 37.28

$\text{Na}_2\text{S} \cdot \text{C}_2\text{H}_5\text{O}$  requires Na = 37.09; S = 25.81;  $\text{C}_2\text{H}_5\text{O}$  = 37.09 per cent.

On heating the substance, which was evidently an alcoholate of sodium monosulphide, alcohol was evolved, and a residue remained, which darkened slightly on further heating, but did not fuse when heated to redness.

A portion of the alcoholate was placed in a flask connected with a Töpler pump, and the vessel was exhausted. The flask was then heated in an oil-bath to  $150^\circ$ , the alcohol being removed continually by absorbing it with phosphoric oxide. A product was obtained which was very faintly buff-coloured, but dissolved in water forming a clear solution, and in hydrochloric acid forming a very slightly opalescent solution. It did not fuse when heated to redness:

0.2231 gave 0.5348  $\text{Na}_2\text{SO}_4$ , Na = 58.77.

0.3360 „ 0.2953  $\text{BaSO}_4$ , S = 40.68.

$\text{Na}_2\text{S}$  requires Na = 58.97; S = 41.03 per cent.

The yield of sodium monosulphide was only small, as it was found necessary to wash the product of precipitation several times with alcohol in order to free it completely from ethoxide, and this occasioned considerable loss of the sulphide.

#### *The Action of Heat on Sodium Monosulphide.*

The following experiments were carried out by heating pure anhydrous sodium hydrosulphide, contained in a small distillation flask, in a bath of sulphuric acid, and, finally, to fusion in a bath of molten solder.

1. *In Dry Air at Atmospheric Pressure.* The substance became slightly yellow at about  $80^\circ$ . Between  $100^\circ$  and  $105^\circ$  the colour deepened rapidly to orange yellow. On further heating, the sub-

stance became darker, and finally fused to an almost black liquid at about  $350^{\circ}$ .

Hydrogen sulphide and sulphur dioxide were evolved during the heating, and the fusion, which on cooling became bright yellow, was immediately decomposed on treatment with hydrochloric acid, a copious precipitate of sulphur, derived partly from polysulphides and partly from oxidation compounds, being produced.

2. *In Dry Hydrogen at Atmospheric Pressure.*—The yellow coloration was again noticeable at  $80^{\circ}$ , and it became distinctly deeper between  $100^{\circ}$  and  $105^{\circ}$ , although not so intense as in the previous experiment. After the substance had fused, the gas in the flask was displaced by dry hydrogen, and was found to be rich in hydrogen sulphide. The fusion was decomposed on treatment with hydrochloric acid, giving a precipitate of sulphur, which, in this case, must have been derived entirely from the polysulphide formed. The polysulphide sulphur was estimated by decomposing a portion of the substance with dilute hydrochloric acid and weighing the precipitated sulphur in a Gooch crucible (Küster and Heberlein, *Zeitsch. anorg. Chem.*, 1905, **43**, 53):

1.1899 gave 0.0074 sulphur. Polysulphide sulphur = 0.62 per cent.

3. *In Dry Hydrogen Sulphide at Atmospheric Pressure.*—Similar colour changes. Analysis of the fusion showed that the amount of polysulphide sulphur was considerably greater in this case. This is to be expected, as the hydrogen sulphide forming the atmosphere is itself partly dissociated at the temperatures employed:

2.0126 gave 0.0365 sulphur. Polysulphide sulphur = 1.78 per cent.

4. *In a Vacuum.*—Sodium hydrosulphide contained in an exhausted flask, which was plunged into a bath of molten solder at  $100^{\circ}$ , became bright yellow and fused, with evolution of hydrogen sulphide, but when the heating\* was carried out gradually, the substance was completely dissociated into the monosulphide without the production of any yellow colour.

About 5 grams of freshly prepared pure sodium hydrosulphide were placed in a small Jena-glass flask connected to a Töpler pump, a tube of solid potassium hydroxide being interposed between the flask and the pump in order to absorb the hydrogen sulphide evolved. The flask was exhausted, and was then heated in an air-bath, the temperature of which was recorded by means of a thermometer filled with nitrogen. During the heating process the various changes in the appearance of the substance were carefully noted as the temperature was gradually raised. At  $100^{\circ}$  it acquired a peculiar greenish yellow tinge, which first became noticeable round the edges of the substance, but gradually spread throughout the entire mass. At  $180^{\circ}$  the potassium hydroxide in the absorption



tube became moist, indicating that hydrogen sulphide was being evolved. At  $250^{\circ}$  the evolution of hydrogen sulphide was comparatively rapid. The temperature of the bath was gradually raised to  $500^{\circ}$ , and was maintained there for two days. The substance, which was now pale brown, did not fuse at that temperature, but remained in the form of a powder. On cooling, a faintly buff coloured product was obtained, which readily dissolved in water and alcohol, and gave a very faintly opalescent solution on treatment with hydrochloric acid:

0.2416 gave 0.4383  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=58.76$ .

0.2892 „ 0.8754  $\text{BaSO}_4$ .  $\text{S}=41.57$ .

$\text{Na}_2\text{S}$  requires  $\text{Na}=58.97$ ;  $\text{S}=41.03$  per cent.

From the result of the analysis it is evident that the product is sodium monosulphide, and it is therefore possible to bring about the complete dissociation of the hydrosulphide at a temperature not exceeding  $500^{\circ}$ , and, by observing the conditions described, to avoid the secondary reaction which results in the formation of polysulphides.

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### XC.—*The Absorption Spectra of Some Derivatives of the Nitroaminophenols in Relation to their Constitution.*

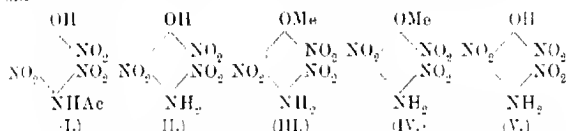
By RAPHAEL MELDOLA and JOHN THEODORE HEWITT.

THE compounds of which the absorption spectra are described in the present paper have been selected for the special reason that they form a natural group, the members of which are comparable among themselves, and also because several of them show remarkable and visible colour changes under the influence of acids and alkalis respectively. With respect to the individual compounds dealt with, picramic acid (2:4-dinitro-6-aminophenol) and isopicramic acid (2:6-dinitro-4-aminophenol) may be considered to have had their constitutions determined long ago so far as concerns the positions of the nitro- and the amino-groups with respect to the hydroxyl group. The methyl ether of isopicramic acid (2:6-dinitro-*p*-anisidine) was described by one of the authors and F. G. C. Stephens in 1905 (T., **87**, 1204). The hydroxyl group of picramic acid appears to be incapable of methylation directly or indirectly.

and all attempts to prepare 2:4-dinitro-*o*-anisidine have hitherto failed. Of the two possible trinitro-derivatives of *p*-aminophenol only one is at present known, the acetyl derivative having been described by one of the authors in 1906 (T., 89, 1935) and the trinitroaminophenol itself in 1909 (Meldola and Hay, T., 95, 1379). Although only one of the two possible trinitro-*p*-aminophenols is known, both of the possible trinitroanisidines have been obtained (Reverdin and de Luc, *Arch. Sci. phys. nat.*, 1909, [iv], 27, 383; Meldola and Kuntzen, T., 1910, 97, 455), and their absorption spectra are given in the present paper.

With respect to the constitution of these trinitro-derivatives, it appears from new evidence which has recently been obtained by M. Reverdin that the formulae of these compounds so far as concerns the position of the third nitro-group will require modification.

The original trinitroacetylaminophenol and trinitroaminophenol were assigned formulae (I and II) representing them as 2:3:5-trinitro-derivatives:



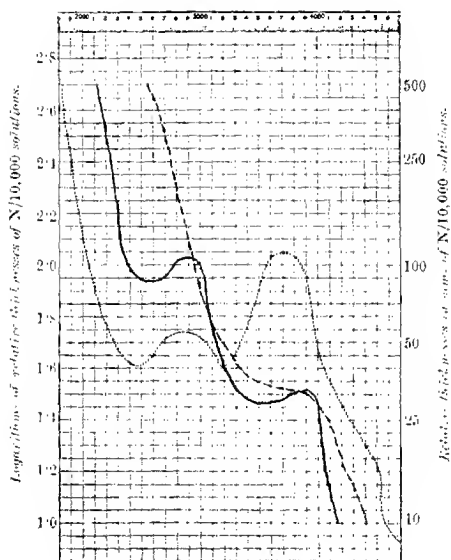
The corresponding trinitroanisidine obtained by the methylation of I and hydrolysis of the acetyl derivative was accordingly given formula III, and the trinitroanisidine of Reverdin and de Luc the alternative formula IV. The evidence on which the 2:3:5-constitution was assigned to trinitroaminophenol, although indirect, was perfectly definite so far as it went. It appears, however, that during the nitration of some of these derivatives of *p*-aminophenol the passage to the trinitro-stage may be accompanied by a quite unsuspected migration of the third nitro-group, and that the trinitroanisidine of Reverdin and de Luc is in reality the 2:3:5-modification (III), whilst the isomeride is the 2:3:6-modification (IV). From this it follows that the known trinitroaminophenol is also the 2:3:6-modification (V), and that the isomeric 2:3:5-trinitroaminophenol (II) yet remains to be discovered. The evidence which has rendered this revision of the position of the third nitro-group will be submitted by one of the authors and M. Reverdin in a later communication, when the experiments bearing on this subject have been completed.

*Absorption Spectra of Dinitroaminophenols and  
Trinitroanisidines.*

*Picramic Acid.*—This compound gives different spectra according to whether it is examined in alcohol alone, in alcohol to which hydrochloric acid has been added, or in dilute aqueous sodium

FIG. 1.

*Scale of oscillation frequencies.*



*Picramic acid:*

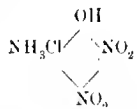
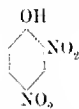
— — — — — *in alcohol with hydrochloric acid,*

..... *in dilute aqueous sodium hydroxide.*

hydroxide. Addition of hydrochloric acid to the alcoholic solution shifts the absorption to the ultra violet end of the spectrum, whilst addition of sodium hydroxide causes the absorption to move in the direction of the red, the colour change which accompanies this shift taking place when the concentration of hydrogen ions in the solution lies between the limits of  $10^{-4}$  and  $10^{-3}$ . Since the colour

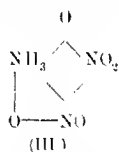
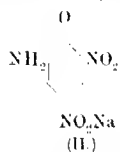
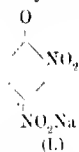
change for 2:4-dinitrophenol also occurs between the same limits, this substance and picramic acid have nearly the same dissociation constants.

Comparison of the absorption spectra of picramic acid and 2:4-dinitrophenol is of interest. The latter compound gives a broad, shallow band with its head at an oscillation frequency of 3400 (Buttle and Hewitt, T., 1909, **95**, 1755) if, before photographing, the alcoholic solution is acidified with hydrochloric acid in order to restrain the ionisation of the phenol. In the case of picramic acid, the band no longer comes to a head, but the shape of the absorption curve shows that there is a chief oscillation frequency about 3400, the curve becoming practically flat at that point. Excess of hydrogen chloride being present in both cases, it may be assumed that the absorptions measured were those corresponding with the respective structures:



As is generally noticed, substitution of hydrogen by the ammonium chloride group,  $\text{NR}_3\text{Cl}$  (here  $\text{R} = \text{H}$  or alkyl; compare methyl-green, etc.), has very little influence on the absorption.

Addition of alkali has an even more marked effect on the absorption of picramic acid than on that of 2:4-dinitrophenol. In the latter case the head of the band (now well in the visible spectrum) is found at 2700, but with the introduction of an amino-group the shift is as far as oscillation frequency 2480. In these cases one is presumably dealing with salts having the constitutions I and II, or



their respective ions, the "auxochromic" effect of the extra amino-group being quite pronounced. In alcoholic solution the picramic acid gives an absorption spectrum differing from that given either in acid or alkaline solution, although it resembles the latter more closely than the former. We are inclined to attribute to the acid, which is not likely to be dissociated very highly in alcoholic solution, a formula such as III, which represents it as an internal salt (compare Green and Rowe, *loc. cit.*, p. 511).

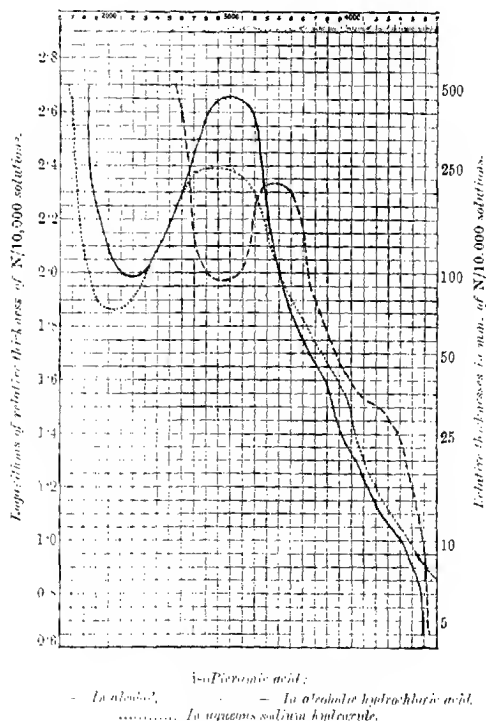
*isoPicramic Acid.* *isoPicramic acid* may be compared in a similar

manner with 2:6-dinitrophenol, similar relationships as to oscillation frequency being observed in this case:

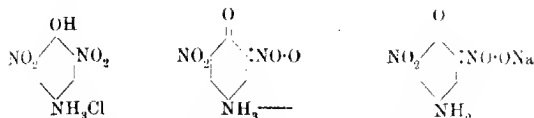
	2:6-Dinitrophenol	isoPieramic acid.
Alcohol + HCl .....	2950	2950
Alcohol .....	—	2200
Aqueous NaOH .....	2300	2000

FIG. 2.

Scale of oscillation frequencies.

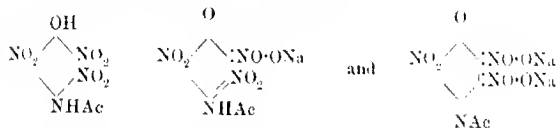


Arguments such as those which have been used for 2:4-dinitrophenol and pieramic acid lead to the conclusion that the structures in acid, neutral, and alkaline solutions may be represented by the following formulæ:

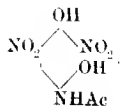


Although the absorption spectra in neutral solution and in excess of alkali do not appear very markedly different on the plotted diagram of absorption, the change is very striking to the eye, since, when the alkaline salt is formed, the yellow part of the spectrum is blotted out, and the colour changes from orange to a splendid purple-red. This property of the compound has suggested its utilisation as an indicator, for which purpose it appears to offer in some cases advantages over the indicators in general use (Meldola, Hale, and Thompson, *Chemical World*, 1912, 1, 327). The change occurs when the concentration of hydrogen ions is reduced from  $N \times 10^{-5}$  to  $N \times 10^{-6}$ . The change orange to nearly colourless (salt formed with hydrochloric acid) occurs on increasing the concentration of hydrogen ions from  $N \times 10^{-2}$  to  $N \times 10^{-1}$ .

*2:3:6-Trinitro-4-acetylaminophenol*.—The absorption spectra of this compound in alcoholic solutions containing excess of hydrogen chloride, sodium acetate, and sodium hydroxide respectively have been previously recorded (T., 1910, 97, 456). The first solution evidently contains the non-ionised compound, the second a non-hydrolysed but easily ionisable monosodium salt, and the third probably a disodium salt easily hydrolysed on dilution. The constitutions of these substances are probably



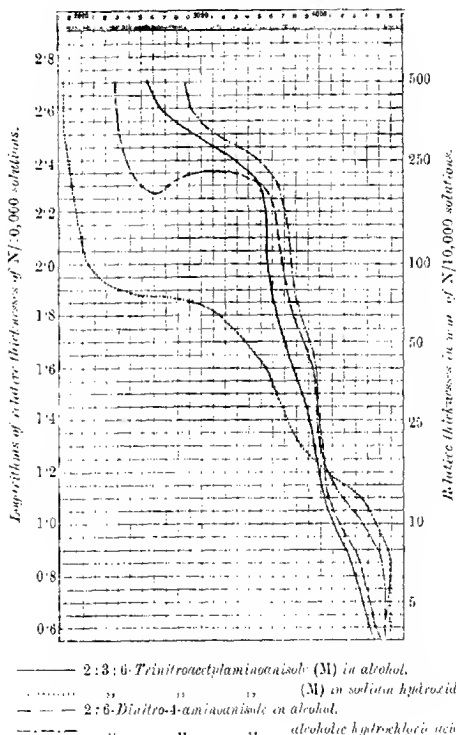
respectively. The colour change corresponding with the formation of the monosodium salt occurs on reducing the concentration of the hydrogen ions from  $N$  to  $N \times 10^{-1}$ ; the second colour change with formation of dibasic salt between  $N \times 10^{-11}$  and  $N \times 10^{-12}$ . At the time of the former publication no proof was given that the second colour change was not accompanied by removal of the "mobile" nitro-group (3) with the formation of a salt of a dinitro-acetylaminoresorcinol:



That this is not the case was shown by the following experiment. Trinitroacetylaminophenol was dissolved in sufficiently concentrated alkali to give the purple solution; this was then acidified and

FIG. 3.

*Scale of oscillation frequencies.*



extracted with ether. The solid residue left on evaporating the solvent resembled the original phenol in appearance, and in solution gave the colour changes for the same alterations in concentration of hydrogen ions.

*Methyl Ether of 2:3:6-Trinitroacetylaminophenol.*

The absorption curve of this compound dissolved in alcohol shows no marked band (Fig. 3), but when an excess of sodium hydroxide is added to the alcoholic solution so that the concentration of hydrogen ions is reduced from  $N \times 10^{-9}$  to  $N \times 10^{-10}$  a marked colour change, presumably attended by salt formation, is observed (Fig. 3). This change is not accompanied by hydrolysis, as was proved by adding alkali to an alcoholic solution until the deep colour was produced, acidifying the liquid, and recovering the substance thus precipitated. The latter, after being washed and dried, melted at the same temperature as the original material, and, mixed with it, did not depress its melting point.

Curves 3 and 4 of the same figure give the absorption spectra of dinitroanisidine in alcoholic solution and in alcohol to which hydrochloric acid has been added. In the first of these a not very persistent band will be noticed with its head at an oscillation frequency of about 2600, so that addition of hydrochloric acid appears to inhibit the bathochromic effect of the amino-group, and the curve of absorption closely resembles that of the corresponding trinitroacetylaminobenzole. This result is quite in agreement with the constitutions;



the effect of the amino-groups being inhibited in one case by salt-formation, in the other by acylation; the third nitro group might be expected to have no very profound influence.

*Methyl Ether of Reardon's 2:3:5-Trinitroaminophenol and of the Corresponding Trinitroacetylaminophenol.*

The absorption curves of these two substances in alcoholic solution are shown in Fig. 4. The marked selective absorption of the non-acetylated compound is very noticeable; that of the acetyl derivative, whilst differing from the curve of the isomeric compound, is not altogether dissimilar. In the latter case a deeper colour is produced on addition of alkali, this change being brought about in much the same way, both isomeric acetyl amino compounds showing the change when the hydrogen ion concentration is reduced from  $N \times 10^{-9}$  to  $N \times 10^{-10}$ .



The deep colour and strong selective absorption of the non-acetylated compound are suggestive of its having the constitution of an internal salt:

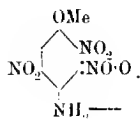
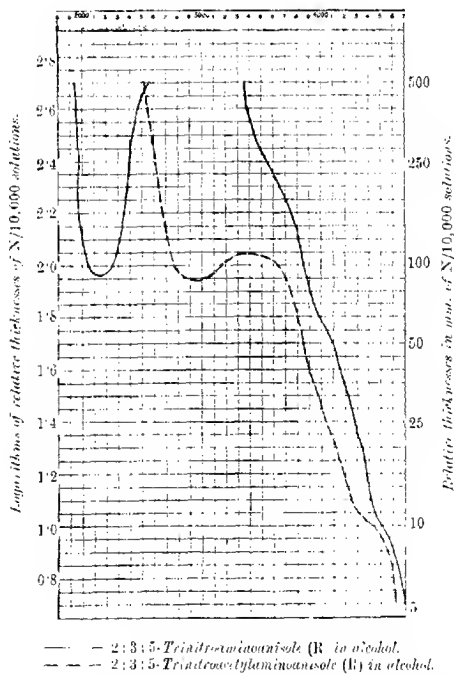


FIG. 4.

Scale of oscillation frequencies.



In favour of this formula it may be pointed out that the amino-group, being between two ortho-nitro-groups, is in an exceptionally favourable position for the formation of such an internal salt.

We desire in conclusion to express our thanks to M. Reverdin, who has kindly supplied us with the specimens of his compounds referred to in the paper, to Miss R. M. Johnson, who took the photographs of the absorption spectra and plotted the accompanying curves, and to Mr. Wm. F. Hollely, who has rendered valuable assistance in the preparation of all the substances other than those prepared by M. Reverdin.

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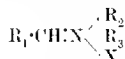
EAST LONDON COLLEGE.

XCI.—*The Carbinol-Ammonium Base Isomerism in Connexion with Azomethine Bases. Part I. Derivatives of Guanaylidene-p-toluidine.*

By CHARLES KENNETH TINKLER.

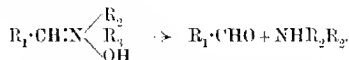
ALTHOUGH in a large number of cases the carbinol-ammonium base isomerism has been investigated in connexion with cyclic bases, only a very limited amount of work has been done in connexion with this isomerism amongst azomethines or Schiff's bases.

During the last ten years this isomerism, as met with in cyclic bases, has been investigated by the author by means of ultra-violet spectroscopy, and following the first paper published on this subject in conjunction with Drs. Dobbie and Lauder on the constitution of cotarnine (T., 1903, **83**, 598), a number of papers in this connexion have been published by the author in conjunction with Dr. Dobbie and independently (T., 1904, **85**, 1007; 1905, **87**, 271; 1906, **89**, 856; 1911, **99**, 1310; 1912, **101**, 1245). The view that cyclic pseudo-bases are more correctly represented as open-chain aldehydes than as closed-chain carbinols is still apparently held by some chemists, and although much of the chemical evidence and the whole of the evidence obtained from the spectroscopic investigation points to the carbinol structure for these bases, it seemed highly desirable to attempt the preparation of a stable quaternary salt of an azomethine compound, with a view to the investigation of alkalis and potassium cyanide on it. If the action of an alkali on such a compound having the linking:

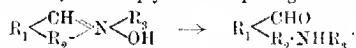


gives rise to an aldehyde, produced by rearrangement of the quaternary ammonium hydroxide, then in the case of an azomethine

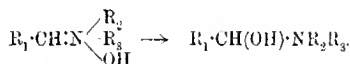
compound such action of alkali should obviously lead to the disruption of the molecule, with the production of free aldehyde and secondary amine:



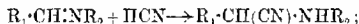
In the case, however, of a cyclic base where  $R_1$  and  $R_2$  are united, even if an aldehyde is produced, it does not lead to the splitting up of the molecule, but simply to the opening of a ring:



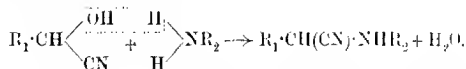
On the other hand, the production of a carbinol from the quaternary ammonium hydroxide of an azomethine compound will not lead to the disruption of the molecule, but give rise to a substance derived from a reduced azomethine base:



It is well known that in a large number of cases the action of potassium cyanide on the quaternary salts of cyclic bases gives rise to a pseudo-cyanide instead of a true salt, from which it appears that the cyanogen group, like the hydroxyl group, is mobile. In all cases, these pseudo-cyanides appear to be derived from the carbinol form of the base by substitution of the cyanogen for the hydroxyl radicle. It has frequently been shown that the addition of hydrocyanic acid to an azomethine compound takes place as follows:



that is, a pseudo-cyanide, or nitrile, is produced (von Miller and Plöchl, *Ber.*, 1892, **25**, 2056; 1898, **31**, 2699; Morgan, T., 1900, **77**, 1210). The same compounds can also be prepared by the action of the cyanohydrin of the aldehyde on the amine from which the azomethine is produced:



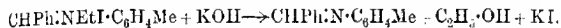
From this method of preparation, the constitution of these substances is apparent.

On account of the ease with which the linking  $:C:N:$  of an azomethine is converted to  $:C \equiv N:$  by the action of hydrogen cyanide, by reduction (O. Fischer, *Ber.*, 1886, **19**, 748), or by the action of Grignard reagents (Busch, *Ber.*, 1904, **37**, 2691), it appeared likely that it would be possible to obtain evidence of the production of a carbinol and a pseudo-cyanide, by the action of a soluble base and

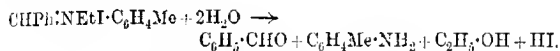
cyanide respectively on the quaternary salt of an azomethine, if such salt could be prepared.

The spectroscopic method of investigation appeared to be especially suitable for this purpose, since the spectra of the nitrile and true salts, and hence of the carbinol and ammonium forms of the base, derived from the azomethine, should be quite distinct.

Attempts to prepare alkyl iodides of Schiff's bases were made by Hantzsch and Schwab (*Ber.*, 1901, **34**, 837), in order that the action of alkalis on these substances might be investigated. The substances which were prepared were, however, extremely unstable. Thus, the most stable compound prepared by these investigators, *p*-tolylbenzylidene-ethylammonium iodide, is decomposed on solution in moist air. With alkali the following reaction took place:



With water the substance is further decomposed, owing to the liberation of hydriodic acid, which causes the hydrolysis of the azomethine:



Hantzsch and Schwab pointed out that, contrary to expectation, no monoethyl-*p*-toluidine was produced. Thus no indication was obtained by these investigators of the production of a pseudo-base of the carbinol form, or even of the secondary amine which would be obtained if the free quaternary ammonium base were converted into free aldehyde and amine. Similar results were obtained by Hantzsch and Schwab in connexion with the somewhat less stable benzylidene-*p*-toluidine methiodide.

In the present investigation the methiodide and ethiodide of benzylidene-*p*-toluidine described by Hantzsch and Schwab (*loc. cit.*) were prepared, and the former was investigated spectroscopically. A solution of this methiodide in alcohol shows comparatively little absorption, owing to the decomposition of the substance, and practically no change in spectra is produced on the addition of soluble base to such a solution. By dissolving the methiodide in an alcoholic solution of sodium hydroxide, the spectra are of the same type as those of the parent base, benzylidene-*p*-toluidine. These results are what would be expected in view of the observations of Hantzsch and Schwab on the decomposition of these quaternary salts.

In the choice of a suitable azomethine base for the attempted preparation of more stable quaternary salts, it appeared desirable to make use of a base having alkyl instead of aryl radicles attached to the nitrogen atom, in order to increase the basicity of the sub-

stance, but in view of the fact that such bases are highly polymerized, this idea was abandoned.

Cinnamylideneaniline\* is described as a Schiff's base which gives rise to a fairly stable hydrochloride and sulphate, which is unusual for these azomethine compounds (Doebner and Miller, *Ber.*, 1883, 16, 1665).

In view of the fact that Hantzsch and Schwab found that the alkyl iodides of benzylidene-*p*-toluidine were more stable than the corresponding aniline compounds, it was decided to prepare cinnamylidene-*p*-toluidine, and to investigate the action of alkyl esters on this base, with the view of the application of such additive compounds to the investigation of the carbinol-ammonium base isomerism.

By the action of methyl iodide on cinnamylidene-*p*-toluidine dissolved in a mixture of ether and benzene, a crystalline mass is produced, which consists apparently of a mixture of the methiodide with a colourless substance. On attempting to crystallise the methiodide from alcohol, the crystalline substance produced is found to be the *hydriodide* of the base, and not the methiodide. This is proved by analysis, and by the identity of the hydriodide prepared by this method and the salt prepared from the base and hydriodic acid. The methiodide of cinnamylidene-*p*-toluidine is therefore decomposed by alcohol, like the methiodides described by Hantzsch and Schwab (*loc. cit.*), but in the case of the present substance the hydriodide is a stable substance, and so separates from the solution. The spectra of an alcoholic solution of the methiodide both before and after recrystallisation differ considerably from those of the parent base, but are in agreement with those of the other salts described later. On the addition of either sodium hydroxide or potassium cyanide to the alcoholic solution of the crude methiodide, the spectra are practically identical with those of the free base, and are quite distinct from those of  $\alpha$ -*p*-toluidino- $\gamma$ -phenylisocrotononitrile,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{CN})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$  (Figs. I and II). If by the addition of soluble base or cyanide to the solution of this quaternary salt, assuming that in a freshly-made cold solution some of the substance is present as quaternary salt, a carbinol or pseudo-cyanide had been produced, the spectra of the solutions should have been in close agreement with those of the above nitrile. It appears therefore that no such carbinol or pseudo-cyanide is produced, but that the quaternary salt is decomposed with liberation of the parent base.

The action of methyl sulphate on cinnamylidene-*p*-toluidine was next investigated. A crystalline substance is produced by the

\* This substance is wrongly described in the literature as "Zinnmatalid."

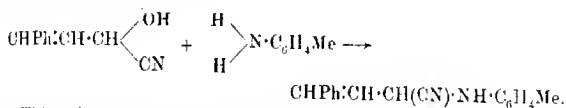
action of methyl sulphate on a solution of the base in a mixture of ether and benzene. After crystallisation from alcohol, however, this substance is found to be cinnamylidene-*p*-toluidine hydrogen methosulphate. As in the case of the methiodide, this is proved by analysis and by the identity of the substance with cinnamylidene-*p*-toluidine hydrogen methosulphate prepared from the base and methylsulphuric acid. The spectra of an alcoholic solution of the substance resulting from the interaction of the base and methyl sulphate both before and after recrystallisation agree with those of the other salts.

On the addition of a soluble base or cyanide, no indication of the formation of either a pseudo-base or cyanide is obtained, the spectra in both cases being identical with those of the parent base.

The crude methiodide and methosulphate are both decomposed by water, giving, on boiling, free aldehyde, amine, and acid like the quaternary iodides of benzylidene-*p*-toluidine described by Hantzsch and Schwab.

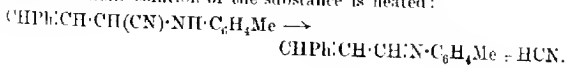
A possible explanation of the remarkable decomposition of these quaternary substances by alkali and water is put forward later in this paper.

The  $\alpha$ -*p*-toluidino- $\gamma$ -phenylisocrotononitrile referred to above was prepared in the usual manner by the action of cinnamaldehydecyanohydrin on *p*-toluidine:



This substance is of interest from the fact that it gives different spectra in ethereal and alcoholic solution, and also that the alcoholic solution does not follow Beer's law.

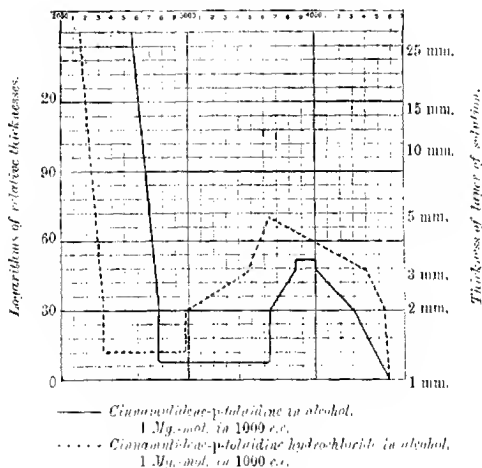
In the case of the pseudo-cyanides of cyclic bases, it has previously been pointed out by the author that these substances are partly converted by alcohol into true cyanides. The spectra of dilute alcoholic solutions of this nitrile show that the solution contains a substance of constitution analogous to that of the free azomethine base, and it is thus obvious that if a cyanide is formed it is not of similar constitution to the ordinary salts of cinnamylidene-*p*-toluidine, for, as previously mentioned, the spectra of these salts differ widely from those of the parent base. It is possible that in this case the pseudo-cyanide simply loses hydrogen cyanide with the formation of azomethine base, as is certainly the case when a dilute alcoholic solution of the substance is heated:



The reverse reaction between hydrogen cyanide and the azomethine base has also been investigated. By treating cinnamylidene-*p*-toluidine dissolved in a mixture of ether and benzene with anhydrous gaseous hydrogen cyanide,  $\alpha$ -*p*-toluidino- $\gamma$ -phenyliso-crotononitrile separates out. The identity of this substance with the nitrile prepared from cinnamaldehydecyanohydrin and *p*-toluidine was established by its melting point, analysis, and absorption spectra.

In addition to the methiodide, hydriodide, methosulphate, and

FIG. 1.  
*Style of oscillation frequencies.*



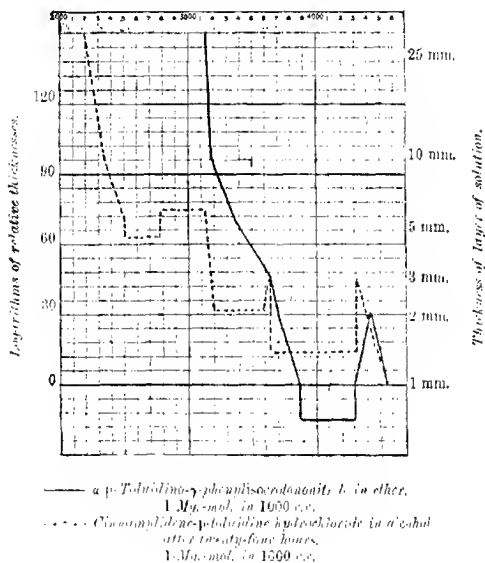
hydrogen methosulphate, the additive compounds of cinnamylidene-*p*-toluidine with hydrochloric, hydrobromic, sulphuric, and nitric acids were prepared and analysed. These salts were prepared for use partly in connexion with the present investigation, and also for investigation in connexion with Hantzsch's theory of "chromoisomerism" (*Ber.*, 1911, **44**, 1783, etc.). It was pointed out by the author (*T.*, 1909, **95**, 921) that the salts which show this phenomenon contain an unreduced pyridine, etc., nucleus, and since it is not shown by such substances as tetrapropylammonium iodide, which do not contain the nitrogen atom in a ring, it appeared of

interest in this connexion to investigate the salts of azomethines, which should contain the linking  $\text{C}:\text{N}^+$ .

The above-mentioned salts of cinnamylidene-*p*-toluidine were prepared by heating the base on the water-bath with a dilute solution of the acid. As a general rule, by such treatment an azomethine base is decomposed into free aldehyde and amine, but although a certain amount of decomposition appears to take place

FIG. 2.

*Scale of oscillation frequencies.*



with cinnamylidene-*p*-toluidine in such circumstances, the crystalline salts separate from the filtrate.

The salts in all cases are produced by the combination of one molecule of the base with one molecule of acid, so that in the case of the sulphate it is the acid salt that is produced. The halogen salts were also prepared by passing the halogen hydride into a benzene solution of the base. All these salts are considerably darker in colour than the parent base, and they also differ widely amongst themselves in their colour intensity. The bearing of these



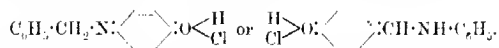
salts on the phenomenon of chromoisomerism will be dealt with in a later communication. In connexion with the present investigation, however, the following results may be mentioned.

The spectra of an alcoholic solution of the hydrochloride differ considerably from those of the parent base (Fig. 1). On the addition of aqueous hydrochloric acid to an alcoholic solution of the free base, the spectra obtained are quite distinct from those of a freshly-made alcoholic solution of the hydrochloride, but are similar to those of an alcoholic solution of this substance which has been prepared some time (Fig. 2). This is explained on the assumption that the addition of aqueous hydrochloric acid to the alcoholic solution of the base causes partial hydrolysis, and this view receives support from the fact that the longer a solution of the hydrochloride has been made the more nearly do the spectra approach those of the colourless solution made by the prolonged action of water on the hydrochloride. In the last case the solution contains cinnamaldehyde and *p*-toluidine hydrochloride, since the spectra of such a solution are in agreement with those of cinnamaldehyde, *p*-toluidine hydrochloride at this dilution showing no absorption.

On the addition of soluble base or cyanide to an alcoholic solution of the hydrochloride, the spectra of the solution are identical with those of the parent base, and not with those of  $\alpha$ -*p*-toluidine- $\gamma$ -phenylisocrotononitrile. This result in both cases is what would be expected in view of the decomposition of the nitrile in dilute alcoholic solution referred to above.

The spectra of a chloroform solution of the hydrochloride undergo no change on keeping the solution.

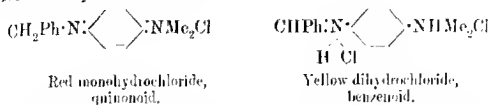
As previously mentioned, all the salts of cinnamylidene-*p*-toluidine are considerably more strongly coloured than the parent base, and in this respect they resemble the hydrochlorides of azomethine bases described by F. G. Pope and Fleming (T., 1908, **93**, 1914) and by F. J. Moore and his co-workers (*J. Amer. Chem. Soc.*, 1908, **30**, 394, 1001; 1910, **32**, 382). These investigators assign a quinonoid structure to certain coloured salts of azomethine bases. Thus Pope and Fleming represent the hydrochlorides of hydroxyazomethine bases as either:



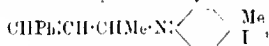
Moore and his co-workers point out that three explanations are possible of the differences in colour of the red monohydrochloride of the Schiff's base benzylidene-*p*-aminodimethylaniline on the one hand, and the yellow parent base and dihydrochloride on the other. The explanation favoured by Moore is that which assigns a

quinonoid constitution to the more strongly coloured salts, and some evidence in support of this theory was obtained by him from the fact that the corresponding meta-substituted compounds do not, as a rule, give rise to red salts.

The hydrochlorides of benzylidene-*p*-aminodimethylaniline are represented by Moore thus:



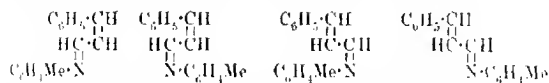
A similar explanation of the coloured salts of substituted azo-compounds was put forward by Hewitt and his co-workers (T., 1909, 95, 1292, 1393, etc.). The possibility of a quinonoid constitution for the salts derived from cinnamylidene-*p*-toluidine must therefore be taken into account. Such a constitution would not only explain the differences in colour between the salts and the parent base, but would also explain why no indication of a pseudo-base is obtained when cinnamylidene-*p*-toluidine methiodide is treated with alkali. Thus, if this substance is represented by the formula:



it would not be expected that a substance of the formula  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\text{Me}$  would be obtained from it by the action of alkali.

The differences in colour shown by a number of Schiff's bases under varying conditions have recently been investigated by Senior and his co-workers (T., 1909, 95, 1943; 1911, 99, 2081; 1912, 101, 1950). These investigators are of opinion that such phenomena may be explained by the molecular aggregation of the bases in the solid state.

It will be noticed that cinnamylidene-*p*-toluidine is capable of existence in four stereoisomeric modifications:



and it is quite possible that the salts are derived from a different isomeride than is represented by the parent base, although, as a rule, the difference between the absorption spectra of *cis*- and *trans*-isomerides is only slight.

## EXPERIMENTAL.

*Cinnamylidene-p-toluidine*,  $C_6H_5 \cdot CH:CH:CH:N \cdot C_6H_4Me$ .

This substance is readily prepared by gently warming a mixture of molecular quantities of cinnamaldehyde and *p*-toluidine. The mass solidifies on cooling, and after drying on a porous plate and crystallisation from alcohol, the base is obtained in pale yellow plates, which melt at  $83^\circ$ . The base is readily soluble in alcohol or benzene, less so in ether or light petroleum:

0.3153 gave 17.6 c.c.  $N_2$  (moist) at  $16^\circ$  and 759 mm.  $N = 6.49$ .

$C_{16}H_{13}N$  requires  $N = 6.34$  per cent.

*Action of Methyl Iodide on Cinnamylidene-p-toluidine.*

The base dissolved in ether containing a little benzene is treated with a slight excess of methyl iodide, and the mixture allowed to remain in the ice-chest for several days. A crystalline mass separates, which, under the microscope, is seen to be a mixture of a coloured and colourless substance. On recrystallisation from alcohol, a reddish-yellow substance is produced, which melts at  $183^\circ$ :

I. 0.1352 gave 0.0901 AgI.  $I = 36.02$ .

II. 0.1040 required 14.78 c.c.  $N/50 \cdot AgNO_3$ .  $I = 36.07$ .

$C_{16}H_{13}N \cdot CH_3I$  requires  $I = 34.96$  per cent.

$C_{16}H_{13}N \cdot HI$  "  $I = 36.36$  "

The hydriodide prepared from the base and hydriodic acid, when mixed with the recrystallised methiodide, produces no lowering of the melting point.

*Action of Methyl Sulphate on Cinnamylidene-p-toluidine.*

The base dissolved in a mixture of ether and benzene is treated with a slight excess of methyl sulphate. After remaining some days at the ordinary temperature, the whole mass becomes practically solid. The substance, after washing with ether, may be crystallised from alcohol. Under the microscope these crystals are seen to be fine, long, rectangular prisms.

The substance, after recrystallisation, is reddish-yellow, and melts and decomposes at  $205^\circ$ :

0.2212 gave 8.1 c.c.  $N_2$  (moist) at  $16^\circ$  and 761.5 mm.  $N = 4.26$ .

0.1634 " 0.1159  $BaSO_4$ .  $S = 9.74$ .

$C_{16}H_{13}N \cdot MeHSO_4$  requires  $N = 4.22$ ;  $S = 9.62$  per cent.

The hydrogen methosulphate of cinnamylidene-*p*-toluidine prepared from the base and methylsulphuric acid is identical in all respects with this substance.

***α-p-Toluidino-γ-phenylisocrotononitrile,***  
 $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}(\text{CN})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}.$

This substance was prepared by the condensation of cinnamaldehydecyanohydrin with *p*-toluidine. After heating the substances in molecular proportions in alcoholic solution for several hours on the water-bath, the nitrile separates on cooling. It is crystallised from light petroleum, in which it is sparingly soluble, and is obtained in colourless leaflets, melting at 119°.

This nitrile may also be prepared by the action of anhydrous gaseous hydrogen cyanide on a solution of cinnamylidene-*p*-toluidine in ether containing a little benzene. After the gas has been passed into the solution for some time, colourless crystals of the nitrile separate, and after washing with ether the substance has the same melting point (119°) as the nitrile prepared by the former method:

0.1414 \* gave 14.3 c.c.  $\text{N}_2$  (moist) at 16° and 742.1 mm.  $\text{N} = 11.46$ .

0.1642 † „ 15.9 c.c.  $\text{N}_2$  „ „ 10° „ 742.3 mm.  $\text{N} = 11.41$ .

$\text{C}_{17}\text{H}_{16}\text{N}_2$  requires  $\text{N} = 11.29$  per cent.

*Additive Compounds of Cinnamylidene-p-toluidine with Acids.*

*Cinnamylidene-p-toluidine Hydrochloride,  $\text{C}_{16}\text{H}_{15}\text{N}, \text{HCl}$ .*

This substance may be prepared by heating the base on the water-bath with dilute hydrochloric acid. After filtering, the salt separates on cooling in fine, reddish-yellow needles. After recrystallisation from alcohol, the substance has a deep yellow colour, and melts at 188–190°. It is sparingly soluble in alcohol or chloroform, and is decomposed by boiling water. The salt may also be prepared by passing gaseous hydrogen chloride into a benzene solution of the base:

0.2997 gave 0.1674  $\text{AgCl}$ .  $\text{Cl} = 13.81$ .

10 c.c. of an *N*/100 solution required 5.0 c.c. 0.999 *N*/50.  $\text{AgNO}_3$ .

$\text{Cl} = 13.76$ .

$\text{C}_{16}\text{H}_{15}\text{N}, \text{HCl}$  requires  $\text{Cl} = 13.77$  per cent.

After heating the alcoholic solution of this salt for twenty hours at 25°, the volume of silver nitrate solution required was unchanged.

The *hydrobromide*, like the hydrochloride, is prepared by warming the base with dilute hydrobromic acid and crystallisation from alcohol, or by passing gaseous hydrogen bromide into a benzene solution of the base.

The substance is darker in colour than the hydrochloride, and melts at 206°.

The percentage of acid in this and the salts described below

\* Prepared by first method.

† Prepared by second method.

may be estimated by warming with excess of standard sodium hydroxide solution and a little alcohol and titration of the excess of alkali:

0.1295 required 7.9 c.c. 1.083 *N*/20-NaOH. HBr = 26.73.

$C_{16}H_{15}N$ , HBr requires HBr = 26.79 per cent.

The *hydriodide* can be prepared by either of the methods employed in the preceding cases. It may be crystallised from alcohol, and has a reddish-yellow colour, which is deeper than that of the bromide; it melts at 183°:

0.1302 required 3.45 c.c. 1.063 *N*/10-NaOH. HI = 36.35.

$C_{16}H_{15}N$ , HI requires HI = 36.65 per cent.

The *hydrogen sulphate*,  $C_{16}H_{15}N, H_2SO_4$ , is obtained in minute crystals by warming the base with dilute sulphuric acid. After recrystallisation from alcohol, the substance melts at 193°:

0.0682 required 7.65 c.c. 1.083 *N*/20-NaOH.  $H_2SO_4$  = 29.8.

$C_{16}H_{15}N, H_2SO_4$  requires  $H_2SO_4$  = 30.73 per cent.

This salt is darker in colour than any of the others.

The *hydrogen methosulphate*,  $C_{16}H_{15}N, MeHSO_4$ , is prepared by warming the base with an aqueous solution of methylsulphuric acid. After crystallisation from alcohol, the substance melts and decomposes at 205°:

0.1636 gave 6.2 c.c.  $N_2$  (moist) at 16.5° and 749.4 mm.  $N$  = 4.32.

0.1543 „ 0.1098  $BaSO_4$ .  $S$  = 9.78.

$C_{16}H_{15}N, MeHSO_4$  requires  $N$  = 4.22;  $S$  = 9.62 per cent.

The *nitrate*,  $C_{16}H_{15}N, HNO_3$ , separates from a solution of the base in warm dilute nitric acid. It is much paler in colour than any of the other salts except the hydrochloride:

0.0895 required 2.8 c.c. 1.083 *N*/10-NaOH.  $HNO_3$  = 21.85.

$C_{16}H_{15}N, HNO_3$  requires  $HNO_3$  = 22.19 per cent.

The *orthophosphate*, *perchlorate*, and *trichloroacetate* can also be prepared by warming the base with a solution of the corresponding acid. The *picrate* is precipitated on mixing benzene solutions of the base and picric acid.

Some of the materials used in this investigation were purchased by means of a grant made by the Research Fund Committee of the Chemical Society, for which the author wishes to express his thanks.

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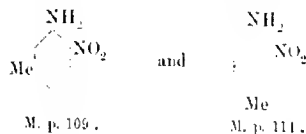
XIV. *The Constitution of Oxadiazole Oxides (Furazan Oxides or Dioxime Peroxides).*

By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

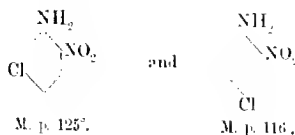
IN a former communication (T., 1912, **101**, 2452) we have published a new method of formation of compounds belonging to the class described originally by Noetting and Kolm and by Zincke and Schwarz as "ortho-dinitroso-derivatives," but regarded later by Forster and Fierz (T., 1907, **91**, 1942) as *o*-quinonedioxime peroxides. This reaction consists in the oxidation of *o*-nitroamines with sodium hypochlorite in an alkaline solution. In view of the improbability of a transference of an oxygen atom from the nitro to the amino-nitrogen, the new method of formation appeared to indicate for these compounds an unsymmetrical structure represented by the formula  $X \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{O}$ , in place of the dioxime-peroxide

constitution,  $X \begin{smallmatrix} \text{N} \cdot \text{O} \\ \text{N} \cdot \text{O} \end{smallmatrix}$ , advocated by Forster and Fierz. On the other hand, these authors have stated that one and the same " $\beta$ -naphthaquinonedioxime peroxide" melting at 127° (identical with Koreff and Ilkink's "1:2-dinitroso-naphthalene" formed by oxidation of  $\beta$ -naphthaquinonedioxime) is obtained on heating either 2-nitro-1-naphthylazoimide or 1-nitro-2-naphthylazoimide,  $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6\text{N}_2$ , thus indicating a symmetrical structure for the product.

In order to obtain further evidence on the point in question, we have submitted to the sodium hypochlorite oxidation the pair of nitrotoluidines:



and the pair of chloronitroanilines:

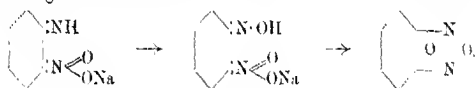


with the object of ascertaining whether isomeric or identical furazan oxides result.

In each case the same oxidation product was obtained from both isomerides, thus confirming Forster and Fierz's observations in the naphthalene series. Symmetrical structure for the furazan oxides is thus definitely established, but in view of the objections already stated to the glyoxime-peroxide formula it appears more probable that the compounds in question have the constitution



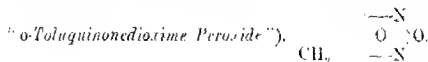
This formula would represent their formation from the nitroamines without requiring the transference of an oxygen atom from the nitro-group, and it also stands in better accord with their chemical properties. The reaction may be regarded as taking place through the intermediate formation of quinonoid compounds, according to the scheme:



#### EXPERIMENTAL.

##### 5-Methylbenzisoaradiazole Oxide.

(Tolufurazan Oxide, Tolufurazan, "Dinitrosotoluene," or



The preparation of this compound from *m*-nitro-*o*-toluidine (m. p. 111°) by oxidation with sodium hypochlorite has already been described in our former paper (*loc. cit.*).

In order to subject *p*-nitro-*m*-toluidine to the same treatment, this base was prepared according to Stadel and Kolb's method (*Annalen*, 1898, 259, 208). Pure *m*-cresol was nitrated in glacial acetic acid solution below 0°, and the portion of the product volatile with steam, nitro-*m*-cresol (m. p. 56°), was converted into the potassium salt and then through the silver salt into the ethyl ether. The nitro-*m*-tolyl ethyl ether obtained melted at 50–51°. To convert this into the nitrotoluidine it was dissolved in a little alcohol and heated with aqueous ammonia in a sealed tube for twelve hours at 200° (heating with aqueous ammonia at 140–150° as prescribed by Stadel and Kolb gave only a small yield). When crystallised

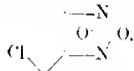
from dilute alcohol the *p*-nitro-*m*-toluidine formed yellow plates melting at 109°.

The oxidation with sodium hypochlorite was effected in alkaline alcoholic solution in a similar manner to that employed for the isomeric base. The product formed white needles melting at 97° (Found, N=18.69), which proved to be completely identical with that from *m*-nitro-*p*-toluidine (Found, N=18.81. Calc., N=18.66 per cent.). It had the same crystalline form, and melted at exactly the same temperature. Mixtures of the two products also had the same melting point.

On reduction with alkaline hydroxylamine the tolufurazan oxide from *p*-nitro-*m*-toluidine gave 3:4-toluquinonediaxime (m. p. 128°: Found, N=18.55. Calc., N=18.43 per cent.) From this the methylbenzisoaxadiazole (tolufurazan) melting at 37° was obtained by distilling the alkaline solution in a current of steam (Found, N=20.91. Calc., N=20.89 per cent.). Both compounds were completely identical with those obtained previously from *m*-nitro-*p*-toluidine.

*Chlorobenzisoaxadiazole oxide.*

(*Chlorobenzfurazan Oxide, Chlorobenzfurozan*),



(1) *Preparation from m-Chloro-o-nitroaniline.*—This base was obtained by Beilstein and Kurbatov's method (*Annalen*, 1876, **182**, 102) by nitration of *m*-chloroacetanilide, saponification of the product and separation from the chloro-*p*-nitroaniline by distillation in a current of steam. When crystallised from benzene it was obtained in golden crystals melting at 125°. The oxidation with sodium hypochlorite was effected in alkaline alcoholic solution in the usual way. The product, which separates on keeping, was crystallised from alcohol, and found to melt at 48°:

0.1809 gave 25.8 c.c. N<sub>2</sub> at 17° and 747 mm. N=16.63.

0.1392 .. 0.1167 AgCl. Cl=20.74.

C<sub>6</sub>H<sub>3</sub>O<sub>2</sub>N<sub>2</sub>Cl requires N=16.43; Cl=20.83 per cent.

(2) *Preparation from p-Chloro-o-nitroaniline.*—This base was obtained in theoretical yield by heating 2:5-dichloronitrobenzene (m. p. 55°), dissolved in sufficient alcohol, with aqueous ammonia under pressure at 190° for eight hours. The product melted at 116.5°. The oxidation with alkaline sodium hypochlorite can be conducted in alcoholic or in aqueous solution. In the latter case the base is dissolved in hot water, rendered alkaline with sodium



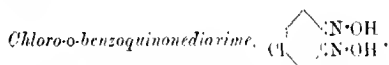
hydroxide, and sodium hypochlorite added until the deep orange red colour disappears. The product which separates on cooling is crystallised from alcohol:

0.1053 gave 14.3 c.c.  $N_2$  at  $14^\circ$  and 758 mm.  $N=16.46$ .

0.1697 „ 0.1418 AgCl.  $Cl=20.66$ .

$C_6H_3O_2N_2Cl$  requires  $N=16.43$ ;  $Cl=20.83$  per cent.

The products are completely identical in properties. They crystallise from alcohol in large, pale yellow, readily soluble crystals, melting at  $48^\circ$ . A mixture of the two compounds also melted at the same temperature.



This compound was obtained by reduction of the chlorofurazan oxide prepared from either *m*- or *p*-chloro-*o*-nitroaniline. The reduction was effected in alcoholic solution with alkaline hydroxylamine. The product was a brown, crystalline powder, melting at  $128^\circ$ , having the general properties of *o*-dioximes:

0.0758 \* gave 10.7 c.c.  $N_2$  at  $17^\circ$  and 746 mm.  $N=16.44$ .

0.0926 † „ 12.7 c.c.  $N_2$  „  $14^\circ$  „ 758 mm.  $N=16.40$ .

0.1018 \* „ 0.0845 AgCl.  $Cl=20.54$ .

0.1426 † „ 0.1184 AgCl.  $Cl=20.54$ .

$C_6H_3O_2N_2Cl$  requires  $N=16.21$ ;  $Cl=20.58$  per cent.



prepared by subjecting to steam distillation an alkaline solution of chlorobenzoquinonediazime (from *p*-chloro-*o*-nitroaniline). The product forms long, white, silky needles, which melt at  $44^\circ$ . It is readily volatile with steam:

0.0743 gave 11.35 c.c.  $N_2$  at  $15^\circ$  and 758 mm.  $N=18.20$ .

0.1202 „ 0.1108 AgCl.  $Cl=22.97$ .

$C_6H_3ON_2Cl$  requires  $N=18.12$ ;  $Cl=22.93$  per cent.

This and other compounds of the same class are probably more correctly represented by formulae of the benzenoid type,  $X\langle\langle\begin{smallmatrix} N \\ N \end{smallmatrix}\rangle\rangle O$ ,

than by those of the quinonoid type,  $X\langle\langle\begin{smallmatrix} N \\ N \end{smallmatrix}\rangle\rangle O$ . The absence of colour, and resistance to reduction and oxidation stand in better accord with the former than with the latter view of their structure.

\* From *m*-chloro-*o*-nitroaniline.

† From *p*-chloro-*o*-nitroaniline.

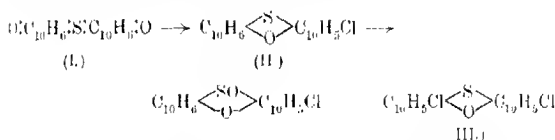
Whilst the dioximes are readily converted into the furazan oxides by oxidation in alkaline solution with sodium hypochlorite, the furazans remain unchanged under this treatment. The latter are also strongly basic compounds, forming readily soluble hydrochlorides.

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### XIII. *Naphthathioxin and iso-Naphthathioxin.*

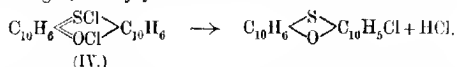
By THOMAS JOSEPH NOLAN and SAMUEL SMILES.

DURING the investigation of the action of acetyl chloride on  $\beta$ -naphthasulphonium-quinone (I), monochloronaphthathioxin (II) was obtained (T., 1912, 101, 715). This substance was converted into the oxide, and thence, by means of hydrogen chloride, dichloronaphthathioxin (III) was prepared:



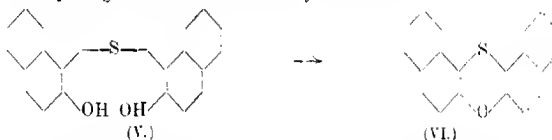
Since naphthathioxin had been previously obtained by the dehydration of  $\beta$ -naphthol sulphide, attempts were then made to synthesise the foregoing chloro-compounds by chlorination of the parental substance. Accordingly, the oxide of naphthathioxin (T., 1912, 101, 714) was converted by the action of hydrogen chloride into the chloro-derivatives. The process yielded a mixture of mono- and di-halogen derivatives, but of these neither was identical with the corresponding substance formed from the quinone. In explanation of this circumstance two alternative hypotheses were available: either that the difference between the two series was solely due to the varying situation of halogen in the naphthalene nuclei, or that the parental thioxin of each was different. The former alternative could only be accepted with some hesitation, for it is in conflict with theoretical views advanced to explain the interaction of the quinone and acetyl chloride (T., 1912, 101, 711). Without repeating the evidence on which these views were founded, it may be remarked that the conclusion was made that at the

penultimate stage the thioxonium chloride is formed (IV), which, losing halogen, finally yields chloro-derivatives of the nucleus:



This has now been fully confirmed by the isolation of the corresponding thioxonium bromide from the interaction of the quinone and acetyl bromide. In the meantime other experiments (this vol., p. 319, and this paper) have shown that also direct halogenation of the naphthathioxin leads to initial products of this thioxonium type (IV); hence, provided that the parental naphthathioxin is the same in the two series, similar orientation of the halogen in the products of the two methods is to be expected. For these reasons it seemed improbable that the former of the foregoing alternatives is correct, and attention was therefore turned to the possibility of the existence of two isomeric naphthathioxins. Experiment has revealed the existence of these substances.

*Naphthathioxin*.—The naphthathioxin hitherto known is obtained by the dehydration of  $\beta$ -naphthol sulphide (V) with phosphoryl chloride (Mauthner, *Ber.*, 1906, **39**, 1340; Christopher and Smiles, *T.*, 1912, **101**, 713). The constitution (VI) of a thioxin has been already assigned to this substance by Mauthner:



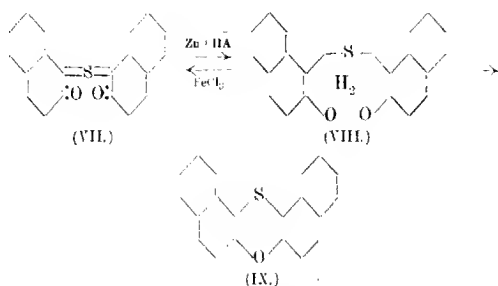
It need now only be said that this structure clearly follows from the fact that the substance is formed by removal of the elements of water from a dihydroxy-derivative of known constitution (V). Moreover, during the process, the hydroxyl groups disappear, and the product assumes the distinctive character which must be expected of a thioxin from analogy to other similar heterocyclic compounds; thus the substance is readily oxidised by cold concentrated sulphuric acid or by ferric chloride in ethereal solution. It yields an oxide, which is readily transformed by hydrogen chloride or bromide into halogen derivatives of the nucleus. Further oxidation yields a sulphone, whilst with bromine the parent substance furnishes highly coloured additive products, to which the thioxonium structure must be assigned. All these reactions find a strict parallel in the thiazin series.

We have now further examined this substance, and a set of four characteristic derivatives has been prepared for comparison

with those obtained from *isonaphthathioxin*. The relations between these substances are summarised in a table given on p. 905, whilst the mode of preparation is described in the experimental part of this paper.

*iso-Naphthathioxin*.—The existence of an isomeride of naphthathioxin has been already indicated by experiments (this vol., p. 347) dealing with the interaction of acetic anhydride and the acetyl derivative of *iso-β*-naphthol sulphide. Other more convenient means of preparing the substance by dehydrating *iso-β*-naphthol sulphide are described in the experimental part of this paper. The melting point of this anhydride of *iso-β*-naphthol sulphide lies only some 15° apart from that of the naphthathioxin derived from *β*-naphthol sulphide; but the lowering in melting point of a mixture of the compounds and the existence of two distinct sets of derivatives shows that the substances are not identical. A summary of these derivatives is given on a subsequent page.

*Constitution*.—The molecular weights of the two substances measured in the same solvent corresponds with the simple formula derived from the sulphides by intramolecular loss of the elements of water. The thioxin structure for this *iso*-anhydride is advanced by the following argument. The presence of the thio-arrangement is demonstrated by the successive formation of a sulfoxide and a sulphone when the substance is treated with oxidising agents. Direct evidence showing the oxide grouping cannot be adduced, but the presence of oxygen in this form may be inferred from the fact that hydroxyl or carbonyl cannot be detected by the usual reagents in the parental substance or its derivatives. In further support of the thioxin structure it must be observed that this anhydride of *iso-β*-naphthol sulphide cannot be qualitatively distinguished by means of its chemical behaviour from naphthathioxin; in fact, both exhibit the characteristic reactions of the thioxin structure, and, so far as our experiments have been carried, only minor quantitative differences in the reactivities of the two substances can be detected, the sulphur in the *iso*-derivative being somewhat less reactive than that in naphthathioxin. For these reasons it is clear that the thioxin structure for this anhydride must be adopted. It now remains to discuss the relative situation of the thioxin complex and the naphthalene nuclei. In previous papers it has been pointed out that since *iso-β*-naphthol sulphide is formed by reducing *β*-naphthasulphonium-quinone (VII), and is oxidised thereto by mild oxidising agents, the positions of oxygen and sulphur in this sulphide must be the same as in the quinone, that is, in the *β*- and *α*-positions respectively, as indicated by the following formula (VIII):



This arrangement is the same as that assigned for other reasons to  $\beta$ -naphthol sulphide (some of these are quoted in T., 1912, 101, 1146, 1420). Without now discussing the ultimate structure of the *iso*-sulphide, it is sufficient to repeat that since the *isonaphthathioxin* is obtained from this by dehydration, it is to be expected that the thioxin arrangement which is formed should occupy the same situation (as in IX) as the several components. Other evidence leading to the  $\alpha\beta$  structure for *isonaphthathioxin* may be adduced from the production of derivatives of this substance from  $\beta$ -naphthasulphonium-quinone (VII), which contains the sulphur and oxygen in these same positions. The quinone is almost quantitatively converted by cold acetyl bromide (this paper) or warm acetyl chloride (T., 1912, 101, 715) into halogen derivatives of *isonaphthathioxin*. Reviewing these facts, it appears that there is as good evidence for accepting the  $\alpha\beta$ -structure for *isonaphthathioxin* as for naphthathioxin.

It may be further remarked that the dinaphthyl structure is not present in the *iso*-derivative because:

(1) This arrangement does not exist in the *iso*-sulphide, since that compound is converted\* into the quinone by loss of only two atomic proportions of hydrogen. Moreover, the *iso*-sulphide is converted into  $\beta$ -naphthol sulphide by reaction with aqueous alkali hydroside.

(2) Naphthathioxin is not converted into *isonaphthathioxin* by oxidation.

All the data thus lead to the conclusion that the skeletons of these two naphthathioxins are identical, and, if this is admitted, it appears impossible to find an explanation of the isomerism without some reference to the state of the naphthalene nuclei contained by the substances. It seems that the sole objection which can be offered against the identity of skeletal structure is the possibility

\* Experiments proving this will be published in a subsequent paper.

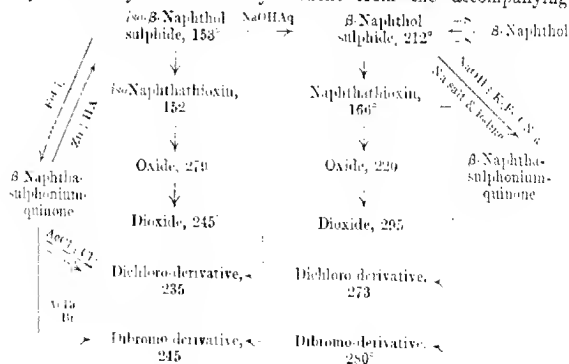
that during the dehydration of either naphthol sulphide some shift of the thio- or oxygen groups may have taken place. In view of previous knowledge it seems highly improbable that such rearrangement should occur in naphthalene derivatives with reagents such as phosphoryl chloride at  $100^{\circ}$ , cold chlorosulphonic acid, or boiling acetic anhydride, which are those used to effect the dehydration. There is still less justification for assuming that in the formation of the *iso*-derivatives from naphthasulphonium-quinone rearrangement should take place with cold acetyl bromide or acetyl chloride. On general grounds, therefore, it seems that this objection against the  $\alpha\beta$ -structure for either substance cannot be urged with success.

Moreover, it may be remarked that to break up the thioxin complex requires much more violent reagents than those employed for dehydrating the sulphides, and hence it is difficult to provide analytical evidence which would be free from the same objection.

We do not, however, wish at present to make further deductions as to the nature of the isomerism of these substances, but prefer to postpone this until the case can be completed by inclusion of the parental sulphides in which the individual characteristics are more pronounced.

It may be of interest here to draw attention to the fact that perusal of the literature will show that already there are known several examples of isomeric naphthalene derivatives in which the substituents occupy the same positions; and a possible explanation of their nature has been foreshadowed by Willstätter (*Ber.*, 1911, 44, 3431).

It remains, finally, to remark on the general relations existing in this group of substances; but a detailed description is unnecessary, since they are sufficiently evident from the accompanying



scheme. On inspection it will be clearly seen that there is an intimate relation on the one hand between the quinone and the *iso*-series, and on the other between the normal series and  $\beta$ -naphthol or  $\beta$ -naphthol sulphide.

The conclusions may be summarised as follows:

(1) Dehydration of *iso*- $\beta$ -naphthol sulphide yields *isonaphthathioxin*, which possesses the simple molecular weight.

(2) This substance is isomeric with the naphthathioxin obtained by dehydration of  $\beta$ -naphthol sulphide; both substances contain the thioxin structure.

(3) Since the parental sulphides contain the thio- and oxygen groups in the  $\alpha$ - and  $\beta$ -positions, it is inferred, with some reservation, that this arrangement is present in the anhydrides.

(4) The *isonaphthathioxin* is closely related to the naphthasulphonium-quinone.

#### EXPERIMENTAL.

*Derivatives of Naphthathioxin*,  $C_{10}H_6 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ O \end{smallmatrix} C_{10}H_6$

It is unnecessary now to describe the preparation of the parent substance of the group, for this has been previously dealt with in another paper (T. 1912, **101**, 714, and Mauthner, *loc. cit.*). In addition to the reactions mentioned in subsequent paragraphs, other characteristics of this naphthathioxin may now be described.

Ferric chloride added to the cold ethereal solution yields a green thioxonium double salt. The substance also is oxidised by cold concentrated sulphuric acid, a blue solution of the sulphoxide being formed. Moreover, when this naphthathioxin is boiled with a concentrated alcoholic solution of picric acid an insoluble reddish-brown picrate is formed; this is decomposed into the original components by treatment with aqueous alkali hydroxide.

A cryoscopic determination of the molecular weight of naphthathioxin was made in molten naphthalene with the following result:

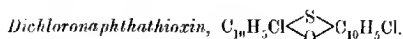
0.220 in 15 of naphthalene gave  $\Delta = 0.345$ . M.W. = 297.

$C_{20}H_{12}OS$  requires M.W. = 300.

The sample of naphthathioxin used melted at 166°.

*Naphthathioxin Oxide*,  $C_{10}H_6 \begin{smallmatrix} SO \\ \diagup \quad \diagdown \\ O \end{smallmatrix} C_{10}H_6$

For the properties of this substance and the mode of preparation from naphthathioxin and nitric acid reference is made to a previous paper (T. 1912, **101**, 714). When a solution of the oxide (and hydrogen bromide) in acetic acid is warmed, the green thioxonium salt is precipitated.



Naphthathioxin oxide was dissolved in hot glacial acetic acid, and then concentrated aqueous hydrogen chloride was added until a faint turbidity appeared. When the mixture was further warmed on the water-bath a mass of yellow needles was rapidly precipitated; and after these had ceased to accumulate, the solid was collected. Preliminary experiments showed that this substance was a mixture of mono- and di-chloronaphthathioxins which was very difficult completely to resolve by fractional crystallisation.

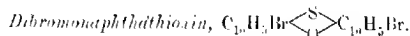
In order entirely to convert the material into the dichloro-compound it was re-chlorinated by a repetition of the foregoing process. Accordingly, the substance was converted into the mixture of oxides by means of concentrated nitric acid (see T., 1912, 101, 714), and these were again treated with hydrogen chloride as described in the foregoing paragraph. The product formed an orange-coloured mass of needles, which contained a small quantity of nitrogenous material. In order to remove this impurity and some oxide of the dichloro-derivative which was possibly present, the material was dissolved in hot tetrachloroethane and reduced in this solution with a small quantity of acetic acid and zinc dust. After a few moments' action the solution was filtered and set aside to cool, when dichloronaphthathioxin separated in an almost pure condition. The substance was further purified by recrystallisation from tetrachloroethane, when it was finally obtained in large, lemon-yellow needles, which melted at  $273^{\circ}$ :

0.1070 gave 0.2540  $CO_2$  and 0.0282  $H_2O$ .  $C = 64.7$ ;  $H = 2.9$ .

0.1670 „ 0.1303  $AgCl$ .  $Cl = 19.3$ .

$C_{20}H_{10}OCl_2S$  requires  $C = 65.0$ ;  $H = 2.7$ ;  $Cl = 19.2$  per cent.

*Dichloronaphthathioxin* imparts a green colour to warm sulphuric acid; it is sparingly soluble in most cold organic media, and is not further chlorinated by a hot mixture of hydrogen dioxide and hydrogen chloride in acetic acid.



A solution of naphthathioxin in warm glacial acetic acid was mixed with a solution of five atomic proportions of bromine in the same solvent. A copious, green precipitate of the thioxonium bromide then separated, but on continued warming on the water-bath this was finally converted into a yellow, crystalline solid. When the change was complete the solid was collected and purified by recrystallisation from hot tetrachloroethane:

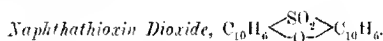


0.1206 gave 0.2330  $\text{CO}_2$  and 0.0262  $\text{H}_2\text{O}$ .  $\text{C}=52.7$ ;  $\text{H}=2.4$ .

0.1548 " 0.1276  $\text{AgBr}$ .  $\text{Br}=35.07$ .

$\text{C}_{20}\text{H}_{16}\text{OBr}_2\text{S}$  requires  $\text{C}=52.4$ ;  $\text{H}=2.2$ ;  $\text{Br}=34.93$  per cent.

*Dibromonaphthathioxin* obtained in this manner melted at  $279-280^\circ$ , and formed broad, well-defined, yellow needles. With warm sulphuric acid it gave the same colour reaction as the dichloro-derivative. When the substance was warmed with excess of bromine in acetic acid, no further bromination of the nucleus was observed.



The preparation of this substance from naphthathioxin by oxidation with potassium permanganate has been previously mentioned (T., 1911, 99, 415); but since the product then obtained was obviously impure, the means by which the pure substance was made may now be given.

One gram of naphthathioxin was dissolved in warm acetic acid, and an equal weight of finely divided potassium permanganate was gradually added with shaking. When the action was complete the liquid was mixed with water, and then, after addition of sulphurous acid, the solid was collected and washed. At this stage a small quantity of the product was treated with concentrated sulphuric acid; the production of a blue colour indicates the presence of sulphoxide, and if this was observed, the whole was submitted to renewed oxidation with half a gram of permanganate.

The substance was again isolated as before, and when dry was recrystallised first from acetic anhydride and finally from hot pyridine, from which it separated in colourless needles:

0.1018 gave 0.2698  $\text{CO}_2$  and 0.0337  $\text{H}_2\text{O}$ .  $\text{C}=72.27$ ;  $\text{H}=3.68$ .

$\text{C}_{20}\text{H}_{12}\text{O}_3\text{S}$  requires  $\text{C}=72.29$ ;  $\text{H}=3.6$  per cent.

Naphthathioxin dioxide is sparingly soluble in most organic media; it does not impart a colour to strong sulphuric acid, and when rapidly heated it melts at  $293-295^\circ$ .

*Derivatives of iso-Naphthathioxin: iso-Naphthathioxin,*



(a) For the preparation of this substance from the acetyl derivative of *iso*- $\beta$ -naphthol sulphide and acetic anhydride reference is made to a previous paper (this vol., p. 340). No improvement to render the yields of the process more certain have been made. It may be added that when only small quantities of the thioxin

have been formed they may be conveniently isolated from the bulk of the unchanged acetyl derivative by warming the whole with an alcoholic solution of picric acid. The insoluble picrate is then collected and decomposed in the usual manner. Instead of employing the acetyl derivative, the *iso*-sulphide may be used in this preparation.

(b) For the preparation from *iso*- $\beta$ -naphthol sulphide and phosphoryl chloride reference is again made to a former paper (I., 1912, 101, 1146). The product was identified by comparison with that given by the sulphuric acid method (see below). The yields are very poor.

(c) *From Chlorosulphonic Acid and iso- $\beta$ -Naphthol Sulphide.*—Six grams of the sulphide were added in small portions to 25 grams of chlorosulphonic acid, which was kept at 0°. During the addition the solution was well stirred, and when all had been added the mixture was kept at the atmospheric temperature for fifteen minutes before being poured into a large bulk of ice-cold water. The subsequent isolation and purification were conducted as described below (d). The product was identified with that obtained by interaction of the sulphide and acetic anhydride [(a) and this vol., p. 340]. The yields are somewhat less than those obtained by the sulphuric acid method.

(d) *From Sulphuric Acid and iso- $\beta$ -Naphthol Sulphide.*—Experiments dealing with the interaction of this sulphide with sulphuric acid have been previously described by Henriques (*Ber.*, 1894, 27, 2999), who states that a dinaphthathiophen melting at 147° is obtained in yield of about 60 per cent. We have frequently repeated this experiment, but have never met with the thiophen derivative, obtaining instead the *isonaphthathioxin* in yields varying between 50 and 60 per cent. of the theoretical. The melting point of this product lies at about 147–148°, but it contains impurity, which is difficult entirely to remove, for the higher melting point (152°) of *isonaphthathioxin* prepared by the acetic anhydride method is reached only after prolonged crystallisation. In preparing the substance we have found most suitable the carefully described conditions adopted by Henriques, but it is advisable to use other means of purification. After the sulphuric acid solution has been mixed with water, the solid is collected and separately treated with excess of aqueous alkali hydroxide; it is then again collected and washed until free from alkali. The dry material is then extracted in a Soxhlet apparatus with hot benzene; this removes the required substance, leaving undissolved a small quantity of blue material. The latter is not easily removed by directly crystallising the crude material from acetic acid; but after

extraction with benzene the product may be readily purified by recrystallisation from alcohol or acetic acid:

0.0964 gave 0.2824  $\text{CO}_2$  and 0.0361  $\text{H}_2\text{O}$ .  $\text{C}=79.8$ ;  $\text{H}=4.2$ .

$\text{C}_{20}\text{H}_{12}\text{OS}$  requires  $\text{C}=80.0$ ;  $\text{H}=4.0$  per cent.

The molecular weight was determined in molten naphthalene:

0.2134 in 15 of naphthalene gave  $\Delta=0.340$ .  $\text{M.W.}=292$ .

$\text{C}_{20}\text{H}_{12}\text{OS}$  requires  $\text{M.W.}=330$ .

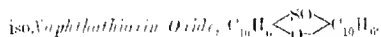
The molecular weight of *iso*- $\beta$ -naphthol sulphide, from which the anhydride was prepared, was also determined:

0.234 in 12.21 of benzene gave  $\Delta=0.300$ .  $\text{M.W.}=319$ .

$\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}$  requires  $\text{M.W.}=318$ .

Analysis of the product obtained by the acetic anhydride method has been previously given (this vol., p. 348). The identity of the substance from the two sources was further established by (a) the identity of melting point ( $152^\circ$ ) taken alone or mixed with one another, (b) by conversion into the same dibromo-derivative (see later), and (c) by conversion to the same dioxide.

*iso*-Naphthathioxin when pure does not immediately yield the blue colour with sulphuric acid, but after some time the colour gradually develops as oxidation to the sulphoxide proceeds. With naphthathioxin the production of the colour is almost instantaneous, and this shows that there is a slight difference in reactivity between the two substances. Other chemical behaviour of this *isonaphthathioxin* is similar to that already given for naphthathioxin; in fact, it is difficult qualitatively to distinguish the two substances. A mixture of *isonaphthathioxin* and naphthathioxin melts indefinitely at about  $120^\circ$ .



(a) *Oxidation with Nitric Acid*.—Like the oxide of naphthathioxin, the *iso*-derivative may be prepared by the interaction of *isonaphthathioxin* with nitric acid (D 1.1). However, it is difficult to purify the product, for it contains nitrogen, not only as nitrate, but also attached to the nucleus. The method is therefore not to be recommended.

(b) *Oxidation with Hydrogen Dioxide*.—Two grams of *isonaphthathioxin* were mixed with 10 c.c. of warm acetic acid, and then 1.5 grams of hydrogen dioxide (30 per cent.) were added. On shaking the warm mixture, the remaining *isonaphthathioxin* dissolved, and in a short time the required substance began to separate. The reaction was completed by further warming, and the crystalline solid was finally collected (1.7 grams) from the cold

liquid. The product was recrystallised from hot pyridine, in which it was readily soluble.

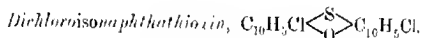
*iso-Naphthathiorin* forms broad, colourless needles, which melt when rapidly heated at 278–279°; if this temperature is maintained a few moments after fusion, profound decomposition sets in:

0.1027 gave 0.2842 CO<sub>2</sub> and 0.0372 H<sub>2</sub>O. C = 75.5; H = 4.0.

C<sub>20</sub>H<sub>12</sub>O<sub>2</sub>S requires C = 75.9; H = 3.8 per cent.

The substance gives an intensely blue solution with sulphuric acid. If aqueous hydrogen chloride is added to the solution in acetic acid the green colour of the thioxonium salt appears, but on warming this disappears, and gives place to a crystalline precipitate of a mixture of chloro-derivatives. On oxidation it is converted into the dioxide. These reactions indicate the presence of the thionyl group.

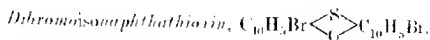
The nitrate is much more soluble than that of naphthathioxin oxide (T. 1912, 101, 714).



(a) *From β-Naphthasulphonium-quinone*.—The preparation of the substance from this source has already been fully described (T. 1912, 101, 716).

(b) *From iso-Naphthathiorin Oxide*.—The mode of preparation from the oxide by means of hydrogen chloride was the same as that described for dichloronaphthathioxin (see above). The product was identified with that made from the quinone (a) by means of the melting point of a mixture (235°).

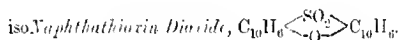
(c) *From iso-Naphthathiorin*.—This substance was dissolved in hot acetic acid to which a small quantity of acetyl chloride had been added. Then hydrogen dioxide in slight excess of that required by theory was added. After the lapse of a few minutes more acetyl chloride was added to the hot mixture, which was then warmed on the water bath for half an hour. The copious precipitate was collected and recrystallised from hot tetrachloroethane, when dichloroisomaphthathioxin was obtained in yellow, thread-like crystals, which melted at 235°, whether heated alone or mixed with a sample made from the quinone. (Found, C = 64.61; H = 2.9. C<sub>20</sub>H<sub>7</sub>OCls requires C = 65.0; H = 2.7 per cent.)



(a) *From iso-Naphthathiorin*. The preparation from isomaphthathiorin obtained from the *iso*-sulphide with acetic anhydride has

been fully described in a former paper (this vol., p. 349). The process has been carried out with a sample prepared by the sulphuric acid method, and the products from the two sources were identical (u. p. 245°).

(b) *From Naphthasulphonium-quinone*.—The same dibromo-derivative may be prepared from this quinone by (i) reaction with bromine in acetic anhydride, or (ii) bromination of the product obtained from the quinone and acetyl bromide. Full details of the processes have been previously given (this vol., p. 351). It is, however, important to add that on repeating the latter preparation (ii) we have been able to isolate the thioxonium bromide, which according to theory (see T., 1911, 99, 976; 1912, 101, 711) should be formed at the penultimate stage of the reaction. In these later experiments it was found that if the solution of the quinone in acetyl bromide was kept at the atmospheric temperature it solidified to a mass of the green thioxonium salt. This was collected, washed, and then boiled with acetic acid, when the impure monobromoisonaphthathioxin described in a previous paper was obtained. As before (this vol., p. 751) this melted at about 178°, and on analysis was found to contain from 1 to 1½ per cent. of bromine in excess of that required by theory. Bromination gave dibromoisonaphthathioxin.



The preparation of this substance from (a) *isonaphthathioxin* or (b) the oxide thereof was conducted precisely as described above for naphthathioxin dioxide. It may be added that the same substance was obtained whether the thioxin employed had been made from the *isosulphide* either with sulphuric acid or acetic anhydride. The product was crystallised first from acetic anhydride and then from hot pyridine:

0.1018 gave 0.2681 CO<sub>2</sub> and 0.0355 H<sub>2</sub>O. C=71.83; H=3.8.

C<sub>20</sub>H<sub>12</sub>O<sub>2</sub>S requires C=72.29; H=3.6 per cent.

*iso-Naphthathioxin dioxide* forms colourless plates, which melt at 244°. A mixture of this substance with naphthathioxin dioxide melted indefinitely between 225° and 235°.

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XIV.—*Studies of Dynamic Isomerism. Part XIV.  
Successive Isomeric Changes in Camphorcarboxyl-  
amide and Camphorcarboxypiperidide.*

By THOMAS MARTIN LOWRY and WALTER HAMIS GLOVER.

IN nearly every case in which mutarotation curves have been examined, they have been found to conform more or less closely to the requirements of a simple unimolecular law. Special interest attaches therefore to the study of any substance which provides an exception to this well-established rule.

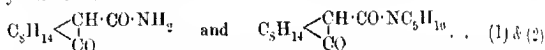
Preliminary observations of the amide and piperidide of camphor-carboxylic acid (P., 1910, **26**, 162) showed that these substances behaved in a totally different manner as compared with all that had been studied in previous papers of the present series. Our attention was specially attracted to a "period of induction," during which the rotatory power of the solutions remained practically constant, and to a "point of inflexion," which indicated that the velocity of change increased gradually to a maximum before the usual decrease of velocity set in.

A mathematical investigation, carried out in collaboration with Mr. W. T. John (T., 1910, **97**, 2634), showed that curves possessing these characteristics might be produced by two successive isomeric changes, of which only the second was accompanied by any marked alteration of rotatory power. At the same time, however, the existence of certain very marked limitations was established. Thus it was discovered that the point of inflexion must occur at a very early stage of the action, since the maximum velocity must be reached before the change had proceeded to the extent of 26.4 per cent. of its total range. A similar limitation was found as regards the slope of the tangent at the point of inflexion. If the tangent were produced to cut the horizontal lines representing the initial and the final rotatory powers of the solution, it was shown that the ratio of the intercepts on these two lines could not in any circumstances exceed a maximum value of 0.0939.

These limiting figures were, however, exceeded in the case of the very first curves that were plotted for the mutarotation of the piperidide in benzene (see the full curves *a* and *b* of Fig. 21. Two curves were plotted, which coincided with one another with remarkable accuracy. These did not reach a point of inflexion until the change had covered some 35 per cent. of its total range, whilst the "ratio of the intercepts" was as high as 0.140. Whilst, therefore, the general character of the curves was similar to that which would

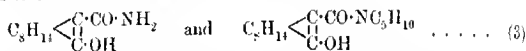
be produced by two successive isomeric changes, it was clear that the cases which were being investigated were more complex, and probably involved more than two changes and more than three isomerides.

No difficulty was experienced in accounting for the complexity of these actions. In the paper in which they were first described (T., 1912, 101, 1902), the amide and piperidide were represented by the conventional formulæ:

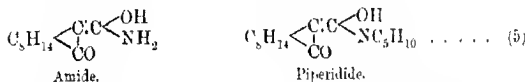
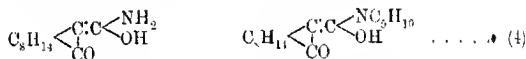


Each of these formulæ, however, may represent either the  $\alpha$ - or the  $\alpha'$ -compound, a type of isomerism that has been fully investigated in the case of the halogen derivatives of camphor (Kipping, P., 1905, 21, 125; Lowry, T., 1906, 89, 1033).

The enolic modifications:



(which provide the most obvious mechanism for the interconversion of the  $\alpha$ - and  $\alpha'$ -diketones formulated above) should exist in only one form; but this is no longer true of the enols of the hydroxy-methylenecamphor type, each of which may exist in two well-defined stereoisomeric forms, thus:



In addition to these five isomeric forms, three additional modifications are rendered possible in the case of the amide by converting the  $\cdot\text{CO} \cdot \text{NH}_2$  group into  $\cdot\text{C}(\text{OH}) \cdot \text{NH}$ . As, however, the isomerism of the amide does not appear to be more complex than that of the piperidide, it is scarcely necessary to consider these in detail.

This multiplicity of possible isomerides is not altogether exceptional; for instance, dextrose and galactose may be represented by at least four formulæ, benzoylcamphor, hydroxymethylenecamphor, and aminomethylenecamphor by five formulæ analogous to those given above, and nitrocamphor might be represented in not less than seven different ways. In most cases, however, there are one or two isomerides, such as the normal and pseudo-forms of nitrocamphor, which predominate to such an extent that all the others may be left out of account in seeking to interpret the mutarotation phenomena. In the two cases now under consideration, there are

evidently several isomerides which do not differ very greatly in stability or importance; the successive isomeric changes proceed with comparable velocities, and each exerts a distinct influence on the form of the mutarotation curve, as, for instance, in curve *f* (Fig. 2), where the effects of three such changes can be seen distinctly. The unusual precautions which have to be taken to crystallise out a homogeneous substance from such complex solutions are referred to later in the paper.

One further cause of complexity must be referred to at this point. The isomeric changes of the amide and piperidide appear to depend, as in the case of nitrocamphor, on the presence of traces of alkaline (?) impurities, apart from which the different isomerides would be quite stable even in solution. The relative quantities of the catalyst vary enormously, and exert a very large influence on the time-scale of the mutarotation curves. Thus in a clean silica tube, a solution of the piperidide in benzene gave a mutarotation curve, which showed that the change was half-complete in eighty hours; in a silica tube that had become contaminated with a trace of alkali, the corresponding period was reduced to three hours. A much more serious effect is seen in the influence of these impurities on the form (as distinguished from the scale) of the curves. The mutarotation curves for solutions of the piperidide in benzene always showed a well-marked period of induction, indicating clearly that the first of the successive changes was not accompanied by any marked alteration of rotatory power. The relative magnitude of the period of induction, however, varied considerably in the different curves; a solution which was observed in a clean silica tube showed a period of induction extending over two hours, the change being half-completed in 160 hours, a ratio of 1 to 80; in an alkaline silica tube the corresponding times were half an hour and three hours, and the ratio 1 to 6. The period of induction in the well-cleaned but still "dirty" tube is exaggerated by the gradual absorption of impurities, but it cannot be attributed entirely to this effect, as no such period was observed when alcohol or heptane was used as solvent, nor when experiments were made with the amide instead of the piperidide.

#### EXPERIMENTAL.

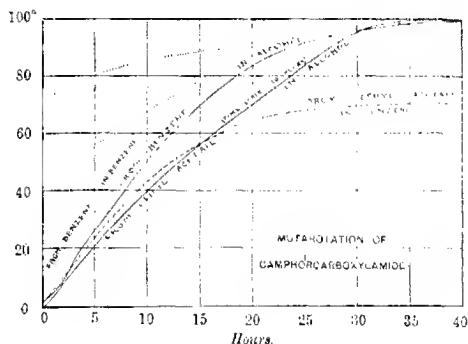
##### *Mutarotation of the Amide.*

Great difficulty was experienced in preparing the amide in such a form that only one of the isomerides was contained in the finished product. The pearly scales which usually separate from solution varied in rotatory power from  $[\alpha]_{461}^{20} + 40^\circ$  to  $+70^\circ$ , and were evidently not homogeneous. It was hoped that homogeneous



material might be obtained by soaking these minute crystals in heptane, and by extracting them repeatedly with this solvent; but when well-formed crystals of the amide were at last obtained from ethyl acetate by slow evaporation, it was found that these attempts had been unavailing, and that the pure amide was practically devoid of rotatory power. This conclusion was confirmed by the examination of crystals which had separated from benzene in well-formed tablets, but which became opaque too quickly to allow of goniometric examination; these were found, like the crystals from ethyl acetate, to be almost entirely inactive. Mutarotation curves for the crude amide, purified by ordinary methods and dissolved in alcohol, are shown by dotted lines in the upper portion of Fig. 1; the corresponding curves for homogeneous material, crystallised from benzene

Fig. 1.



and from ethyl acetate and dissolved in alcohol as before, are shown by full lines in the same figure. The broken line shows the mutarotation of a homogeneous specimen of the amide, crystallised from ethyl acetate and dissolved in benzene; the dotted line in the lower part of the figure represents the mutarotation in benzene of a somewhat less pure specimen which had been prepared by allowing a solution in benzene to evaporate to dryness.

All the curves are marked by two characteristic features: (1) a long run during which the curve is either straight or much less curved than the unimolecular law would require; (2) an initial loop, in which the curve droops away from this line, but returns to it in the course of two or three hours. Both features point to the occurrence of successive isomeric changes. The initial loop appears to correspond with the period of induction of the piperidine, and

suggests that the first product of change is a substance of relatively small rotatory power. The straightening out of the curve would result naturally from the occurrence of a series of changes, each accompanied by an increase of rotatory power. The effect would be to stimulate the growth of rotatory power by a fresh isomeric change, just as it was beginning to flag in view of the approaching completion of the preceding changes. Two successive changes would probably not suffice to account for the form of the curves, but it is evident that the appearance of a third or fourth product of change might stimulate the growth of rotatory power at still later periods, and so keep the curve nearly straight almost to the end of the action.

The numerical data for the three most important curves are reproduced in table I:

TABLE I.—*Mutarotation of Camphorcarboxylamide.*(a) *Cryst. Ethyl Acetate, Diss. Alcohol (5 grams/100 c.c.)*

Time (hours)	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0	1.5	2.0	2.5
[ $\alpha$ ] <sub>D</sub> .....	-0.2	+0.1	0.2	0.3	0.4	0.6	1.1	1.4	2.5	3.7	4.8
Time (hours)	3.0	3.5	4.0	4.5	5.0	8.0	9.0	10.0	11.0	12.1	14.2
[ $\alpha$ ] <sub>D</sub> .....	5.9	7.1	8.2	9.4	10.4	17.2	19.0	21.0	23.3	25.8	29.3
Time (hours)	22	26	30	33	34	36	48	50	51	52	53
[ $\alpha$ ] <sub>D</sub> .....	43.4	50.3	56.4	60.7	62.3	64.8	81.1	84.0	85.4	86.5	88.3
Time (hours)	54.5	56	58	59.4	61	71	83	Final			
[ $\alpha$ ] <sub>D</sub> .....	90.3	91.8	93.8	94.7	96.0	99.6	100.1	100			

(b) *Cryst. Benzene, Diss. Alcohol (5 grams/100 c.c.)*

Time (hours)	0.1	0.2	1.0	2.4	3.1	3.5	4.0	4.5	4.8	6.0	7.0
[ $\alpha$ ] <sub>D</sub> .....	+2.3	2.7	1.5	11.8	16.8	19.2	21.6	24.3	25.9	31.4	36.0
Time (hours)	7.1	8.0	9.0	12.4	15.4	17.6	19.0	20.1	21.0	22.0	24.0
[ $\alpha$ ] <sub>D</sub> .....	38.3	41.3	46.5	60.4	70.7	77.3	80.1	84.0	85.5	87.1	90.1
Time (hours)	25	26	28	30	32	42	Final				
[ $\alpha$ ] <sub>D</sub> .....	91.3	92.9	94.7	96.0	97.0	99.6	100.6				

(c) *Cryst. Ethyl Acetate, Diss. Benzene (5 grams/100 c.c.)*

Time (hours)	0.1	0.2	0.4	0.6	0.8	1.0	2.0	3.0	4.0	5.0	6.0	7.0
[ $\alpha$ ] <sub>D</sub> .....	1.5	2.0	2.9	3.6	4.7	5.5	19.1	15.0	19.9	24.1	28.7	32.6
Time (hours)	8.0	10.0	12.0	13.3	23.0	25.0	28.4	31.0	36.0	48.0	61.0	96.0
[ $\alpha$ ] <sub>D</sub> .....	36.5	43.4	49.2	52.4	67.4	68.0	69.7	71.0	70.9	72.7	73.8	74.4

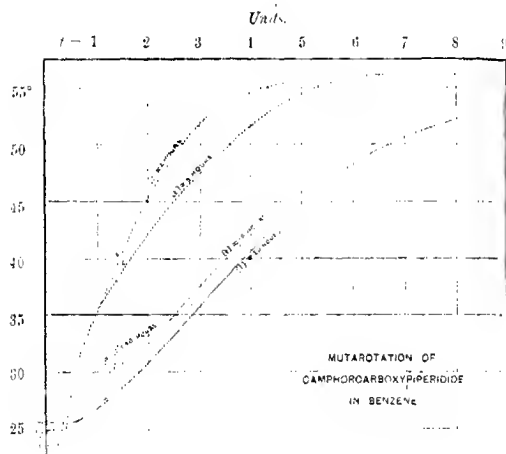
*Mutarotation of the Piperidide.*

The first experiments on the mutarotation of the piperidide were made with material which had been crystallised from alcohol, then dissolved in clean benzene, and transferred to a clean silica polarimeter tube for observation. Two series of experiments were made, as shown by the data of table II (a) and (b), and the full curves

of Fig. 2. After the first few hours the curves run together with a closeness that is quite exceptional in work of this kind. The curves are particularly smooth and regular in appearance, with a well-marked period of induction; it was, indeed, the graceful character of these two curves that supplied the inducement to undertake the mathematical investigation already referred to.

The well-marked, crystalline character of the piperidine used in these first experiments created the impression that no important alteration would be effected by recrystallising the substance from ethyl acetate and using the well-formed crystals (prepared with fur

FIG. 2.



greater ease than in the case of the amide) for the mutarotation experiments. This anticipation was not realised. The initial specific rotatory power of the homogeneous crystals was, indeed, practically the same as that of the less well-defined material that had separated from alcohol. The mutarotation curves, however, differed in a remarkable degree, and showed conclusively that the constancy of specific rotatory power was not due to the complete purity of the earlier material, but to the fact that the isomeride that had been carried down with the crystals was substantially identical in specific rotatory power with the main constituent; the existence of such an isomeride had already been shown to be neces

may to explain the occurrence of a period of induction in these solutions.

Homogeneous material was finally prepared by crushing the well-formed crystals that had separated from ethyl acetate, stirring for several hours with heptane, draining, and drying in the air. Two entirely distinct samples were used, and each solution was examined both in a clean glass polarimeter tube and in a silica tube that had become fouled with alkali. The rapid mutarotation in the foul silica tube is shown by the dotted curves of Fig. 2 and the numbers given in table II (c) and (e). The glass tube, which appears to have been exceptionally clean, gave the slow mutarotation curves represented by the broken lines of Fig. 2 and the data of table II (d) and (f).

TABLE II.

*Mutarotation of Camphorcarboxypiperidine.*

(a) *Cryst. Alcohol, Diss. Benzene (5 grams/100 c.c.),  
Clean Silica Tube.*

Time (hours)	0.05	0.6	1.0	2.5	5.3	11.0	24.0	34.5	46.0	59.0	70.5
$[\alpha]_{589}$	+24.3	24.1	24.4	24.7	24.8	25.8	27.8	30.3	31.8	36.3	36.0

(b) *Repetition of (a), with Same Specimen of Piperidine.*

Time (hours)	0.1	0.4	2	9	12	24	30	36	48	54
$[\alpha]_{589}$	25.8	25.5	25.5	25.3	25.6	27.7	28.7	29.9	32.0	34.2
Time (hours)	61	72	78	81	96	108	132	144	156	
$[\alpha]_{589}$	56.2	39.1	10.6	42.2	44.2	46.5	49.8	51.2	51.2	
Time (days)	7	7.5	8	8.5	9	10	15	21	40	
$[\alpha]_{589}$	52.9	54.3	54.7	51.8	54.8	55.6	56.3	56.9	56.7	

(c) *Cryst. Ethyl Acetate, Diss. Benzene (5 grams/100 c.c.),  
Foul Silica Tube.*

Time (hours)	0.4	0.6	1.0	1.5	2.0	2.1	2.2	2.3	2.5	2.6	3.6
$[\alpha]_{589}$	23.5	23.5	23.5	24.0	24.7	26.2	27.0	28.0	28.5	29.9	34.2
Time (hours)	3.9	4.5	4.9	5.5	6.0	6.5	7.0	8.0	9.0	10.0	11.0
$[\alpha]_{589}$	33.0	33.8	35.4	37.3	37.4	38.0	38.8	40.2	41.9	42.1	43.5
Time (hours)	12.0	12.9	20	22	23	26	28	30	33	36	47
$[\alpha]_{589}$	44.3	45.3	51.9	52.8	53.5	55.0	55.6	55.9	56.1	56.3	56.3

(d) *Same Solution, Clean Glass Tube.*

Time (hours)	0.5	0.7	1.0	1.5	2.0	2.3	2.5	3.0	3.5	4.0	4.5	5.0
$[\alpha]_{589}$	24.7	24.7	24.7	24.7	25.0	25.3	25.3	25.4	25.6	25.8	25.7	25.6
Time (hours)	5.5	6.5	8.0	9.0	10.0	11.0	12.0	13.0	22	28	30	33.1
$[\alpha]_{589}$	25.6	25.8	26.3	26.5	26.6	27.0	27.4	27.5	28.0	29.0	29.2	29.6
Time (hours)	36	46.8	54	59	70	73	78	84	94	102		
$[\alpha]_{589}$	39.0	39.9	31.3	31.6	32.4	32.6	33.3	33.7	34.4	35.1		

(c) *Cryst. Ethyl Acetate, Diss. Benzene* (5 grains/100 c.c.),  
*Poul Silica Tube.*

Time (hours)	0.5	0.6	0.75	0.9	1.0	1.1	1.2	1.4	1.5	1.7	5.0
$[\alpha]_{590}$	25.0	25.4	26.3	27.1	28.4	29.2	30.1	31.9	32.2	33.7	35.5
Time (hours)	2.5	3.0	4.1	4.3	4.5	5.0	6.0	7.0	8.0	22.5	
$[\alpha]_{590}$	38.8	40.8	45.4	46.2	47.3	49.1	51.9	53.5	54.6	56.5	

(f) *Same Solution, Clean Glass Tube.*

Time (hours)	0.5	0.6	0.7	1.0	1.5	2.0	3.0	4.6	6.0	8.0	10.0
$[\alpha]_{590}$	25.4	25.5	25.4	25.2	25.3	25.2	25.4	26.4	27.0	28.2	31.4
Time (hours)	21.0	22	27	33	42.5	49	53	65			
$[\alpha]_{590}$	32.8	33.4	36.1	39.3	43.1	45.4	46.6	50.2			

The first solution changed much more slowly than the second in both tubes; but by using different time-scales the curves are brought closely together, and show a very satisfactory agreement in the behaviour of the two samples. The two dotted curves, which represent the rapid mutarotation in the dirty tube, show a very conspicuous period of induction, followed by a period in which the change of rotatory power proceeds with extraordinary rapidity; the remaining portions of the curves show the long, straight run, to which attention has already been directed in the case of the amide, after which the change of rotatory power soon ceases. The two broken curves, showing the slow changes of rotatory power in the glass tube, were not followed to completion, although readings were taken during a period of several days. They show, however, a very important feature, which can scarcely be detected in the two rapid curves, and is altogether obliterated from the full curve for the non-homogeneous material crystallised from alcohol; this feature consists in the appearance of two distinct periods of acceleration, and affords conclusive evidence that the mutarotation is not due merely to one or two isomeric changes, but involves at least three successive changes in the piperide, which must therefore exist in at least four isomeric forms. These changes give rise:

(1) to a period of induction, during which the first form is changing into a second form of equal rotatory power;

(2) a period of acceleration and subsequent retardation, marking the rise and fall of a third isomeride of higher rotatory power;

(3) a second period of acceleration, due to the production of a fourth isomeride of still higher optical activity.

The second period of acceleration is followed by a "straight-run," which may perhaps be caused by the appearance of a fifth isomeride, but on this point it would be unwise to speak dogmatically.

A few experiments were made on the mutarotation of the piperidide in alcohol. The curves appeared to be approximately normal in shape, but the change of rotatory power from  $[\alpha]_{561}^{20} +112^{\circ}$  to  $+118^{\circ}$  was so small that it was not possible to determine accurately the exact course of the mutarotation.

*Improved Methods for Measuring Changes of Solubility.*

The increase of solubility with time was measured in the case of both substances in order to determine the proportion of the most stable form that was present in the final equilibrium. Important improvements on the methods previously in use were effected.

(1) By crystallising the substance from ethyl acetate in order to secure well-crystallised, homogeneous material, and at the same time to eliminate basic impurities, such as ammonia, by converting them into inert products, such as acetamide.

(2) By using Kahlbaum's commercial heptane as solvent; this has the advantage of being chemically inactive and readily freed from moisture and basic impurities by distilling from phosphoric oxide; as compared with the light petroleum previously employed (T. 1904, 85, 1546), it is more homogeneous and less liable to evaporate during stirring and filtration, but still sufficiently volatile to allow the filtered solutions to be evaporated without undue heating.

(3) By adding the finely-powdered solid at intervals of a few seconds, and in quantities of a few centigrams, to the vigorously-stirred solvent through an aperture in the cork at the top of the tube; under these conditions the finer particles, which usually disappear in the first stages of the dissolution, are retained for use in the process of saturation; complete saturation may thus be secured in the course of two minutes, and only a small excess of the solid need be employed.

*Solubility of Amide.*

Very great difficulty was experienced in preparing the amide in a homogeneous form suitable for experiments on solubility.

The first experiments were made with amide crystallised from light petroleum. Three successive extractions gave the following solubilities:

Initial	0.60	Final	0.80	Grams of amide per 100 grams of heptane.
"	0.73	"	0.79	
"	0.38	"	0.74	

In the third experiment observations were made at short intervals after mixing the amide with the solvent, as the change was

evidently a rapid one; the actual figures were: 10 min., 0.41; 20 min., 0.46; 40 min., 0.53; 80 min., 0.68; 160 min., 0.75; 280 min., 0.73; whence by extrapolation 0 min., 0.38. As the material for the third experiment had been stirred for several days with two successive quantities of heptane, then drained, and again washed with heptane, it was thought that the initial value might be accepted as representing the true solubility of the pure homogeneous unchanged amide. It was not, indeed, until experiments with well-formed crystals had reduced the initial value to 0.24 per cent. that the extreme difficulty of securing homogeneous material was realised. This difficulty is shown by a second series of experiments, in which 10 grams of a new sample, which had been purified most carefully by ordinary methods and finally crystallised out from light petroleum, were soaked with heptane for two months before use. Two grams of the product were stirred with heptane during two days, drained, washed, and powdered; again extracted for two days, drained, washed, and powdered; finally half a gram only of the powder, stirred with 200 c.c. of heptane, gave the following values:

Time.....	5 m.	10 m.	20 m.	0.5 d.	2.5 d.	7.5 d.	14.5 d.	50 d.	56 d.	56 d.	Final
Solubility..	0.35	0.37	0.38	0.48	0.48	0.60	0.64	0.75	0.76	0.79	0.77

The remainder of the 2 grams was soaked with heptane during another sixty days, drained, powdered, extracted twice with heptane, again drained, and then gave the following initial values:

(Time.....	0 m.	6 m.	12 m.)	(Time.....	0 m.	6 m.	12 m.)
(Solubility..	[0.26]	0.29	0.32)	(Solubility..	[0.26]	0.31	0.34)

These values agree with those observed when using well-formed crystals, but this agreement was only obtained after operations extending over a period of more than four months.

Experiments with crystals which had separated from ethyl acetate easily gave concordant initial values, but the final values were reached with extreme slowness on account of the efficiency of this solvent in removing the last traces of catalyst from the crystals. The first specimen gave high values for the first two extractions; a third extraction gave during the first twenty minutes the values 0.20, 0.27, 0.32, 0.25; mean, 0.26. A fourth extraction gave:

(Time., .....	5 m.	10 m.	20 m.	2 h.	56 h.)	Initial
(Solubility..	0.24	0.23	0.25	0.30	0.42)	0.21

A second sample gave at the third extraction: 16 min., 0.27; two hours, 0.29; final (several days later), 0.68; at the fourth extraction: 6 min., 0.23; 12 min., 0.23; 18 min., 0.24. A third sample gave at the first extraction of the whole quantity: 5 min.

0.23; 10 min., 0.24; at a second extraction: 5 min., 0.25; at a third and fourth extraction:

{Time .....	5 m.	10 m.	15 m.	20 m.	30 m.	4 d.	{ Initial
{Solubility ...	0.25	0.24	0.25	0.24	0.25	0.59	{ 0.24
{Time .....	1 d.	2 d.	3 d.	4 d.	11 d.	17 d.	{ Final
{Solubility ...	0.27	0.34	0.42	0.46	0.61	0.65	{ 0.66

A fourth sample, which had already given correct initial values, 5 min., 0.24; 10 min., 0.23, was extracted (a) with pure heptane, (b) with heptane containing a trace of ammonia:

a) Without ammonia	{ Time .....	5 m.	1 d.	3 d.	7 d.	18 d.	37 d.	{ Final
	{ Solubility .	0.24	0.34	0.64	0.66	0.64	0.65	{ 0.65
b) With ammonia	{ Time .....	1 d.	3 d.	7 d.	18 d.			{ Final
	{ Solubility ...	0.53	0.58	0.59	0.66	—		{ 0.66

It will be noticed that the ammonia, which was added with an additional quantity of heptane at the end of one day, makes very little difference to the rate of change, but as this particular sample happened to combine a low initial solubility with a rapid rate of change it served to establish finally the correctness of the following values:

Initial solubility.....	0.24
Final solubility .....	0.66
Ratio .....	0.36

### *Solubility of Piperidine.*

The determination of the ratio of the initial to the final solubility proved to be quite as tedious and difficult as in the case of the amide, several score of observations being made with different samples over a period of two years. It will be sufficient, however, to give the data for the last series, by which the ratio was finally established. The following values are for six successive extractions of the carefully purified sample:

{ 5 m. 1.83 }	{ 5 m. 1.90 }	{ 5 m. 1.84 }	{ Initial
{ 10 m. 1.85 }	{ 10 m. 1.87 }	{ 15 m. 1.89 }	{ solubility
{ 5 m. 1.88 }	{ 5 m. 1.87 }	{ 10 m. 1.89 }	{ 1.85
{ 15 m. 1.85 }	{ 15 m. 1.94 }	{ 25 m. 1.92 }	

The following values are in continuation of the last extraction:

(c) Without piperidine	{ 1 d.	3 d.	6 d.	16 d.	21 d.	24 d.	39 d.	{ Final
	{ 2.00	2.05	2.56	4.19	4.12	4.24	4.26	{ 4.20
(d) With piperidine	{ 1 d.	2 d.	4 d.	7 d.	17 d.	22 d.	25 d.	{ Final
	{ 2.26	2.30	3.86	4.12	4.21	4.14	4.12	{ 4.16

In view of the fact that the solution with piperidine was changing several times more quickly than the solution to which no piperidine was added, it was considered safe to assume that the final solubility had been reached when the two curves came together at the end of about a fortnight. After longer periods the piperidine appeared



to undergo some permanent decomposition, giving rise to solubility values very considerably higher than those recorded above; but as the solution with piperidine gave steady values from seven to twenty-five days, no large error is likely to be introduced by taking as the correct values for the piperidide:

Initial solubility.....	1.87
Final solubility .....	4.18
Ratio .....	0.45

The last series of values was more trustworthy than the earlier ones because care was taken to evaporate the solutions at so low a temperature that the piperidide separated in crystals, instead of remaining as a fused or gelatinous mass; it is believed that this point is of some importance in securing accurate weighings.

It should also be added that the difficulty of securing homogeneous material is closely associated with the inflected character of the mutarotation curves; both phenomena are dependent on the existence of several dynamic isomerides of approximately equal stability and on the occurrence of several successive isomeric changes proceeding so slowly as to exert a marked influence on the properties and behaviour of the solutions.

#### *Summary and Conclusions.*

(1) The amide and piperidide of camphorcarboxylic acid give rise to mutarotation curves of remarkable complexity.

(2) This is attributed to the occurrence of at least three successive isomeric changes, involving not less than four isomerides.

(3) The shape, as well as the scale, of the mutarotation curves may be altered by the gradual absorption of a catalytic impurity.

(4) Solubility measurements have shown that the original form persists after dissolution to the extent of about 36 per cent. in the case of the amide and 45 per cent. in the case of the piperidide.

The authors are indebted to the Research Funds of the Chemical Society and of the British Association for grants which have defrayed a part of the cost of the investigation. They desire also to acknowledge the valuable assistance of Mr. H. R. Courtman in carrying the research through its final stages.

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# XIV.—*Quinonoid Addition as the Mechanism of Dyestuff Formation.*

By ARTHUR GEORGE GREEN.

IN 1899 Thiele (*Annalen*, 1899, **306**, 132) advanced an explanation of the capacity for addition exhibited by quinones and quinonoid compounds which was based on his theory of unsaturation and the existence in such compounds of a chain of "conjugate" double linkings. Bucherer in 1907 (*Ber.*, **40**, 3412) further developed this hypothesis, referring to a single type all the reactions by which the dyestuffs of the azine, thiazine, and oxazine series are produced (compare Möhlau and Bucherer, "Farbenchemisches Praktikum"). For some time past I have employed a similar generalisation, of a somewhat more comprehensive character, which appears to supply a ready explanation of the mechanism by which complex dyestuff molecules are built up, not only in the above-mentioned classes, but also in other groups in which substitutive changes are usually assumed (for example, the rosaniline group).

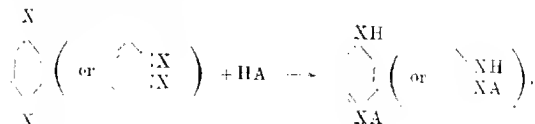
In view of the assistance which such generalisations afford to the student of dyestuff chemistry I venture to give the following account of the form in which I employ this hypothesis.

(1) All quinones and quinone-like compounds, by reason of their high degree of "unsaturation," exhibit a great attraction for hydrogen or equivalent groups, by the assumption of which they can pass into more saturated compounds.

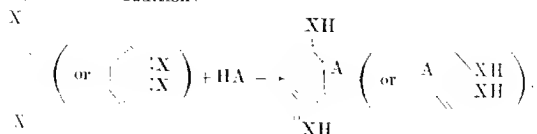
(2) A very large proportion of dyestuff syntheses and the individual steps in such syntheses may be represented as consisting in the linking up of molecules ("Verkettungen") brought about through the attractive forces of quinonoid groups.

(3) Such reactions may occur in two ways, namely:

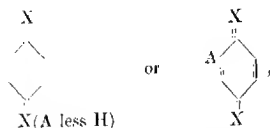
(a) Direct Addition:



(b) Indirect Addition:



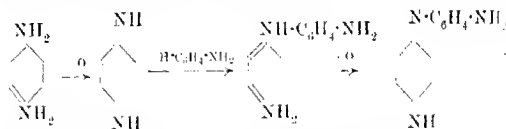
(4) In the presence of an oxidising agent, such as chromic acid, a chlorate, atmospheric oxygen, or another quinonoid compound, the above additive products are again converted into quinonoid derivatives,



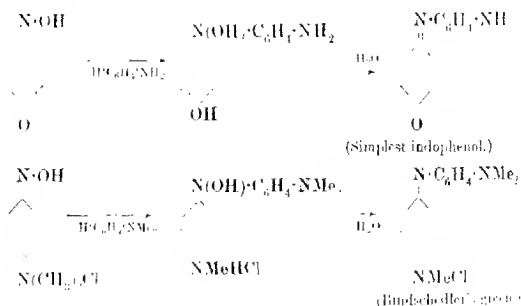
which under suitable conditions are ready to react again in the same way, with production of compounds of still greater complexity. Such alternate additions and reoxidations may occur several times in succession, thus producing (as in the aniline-black and induline series) very complex molecular structures.

#### *Direct Quinonoid Addition.*

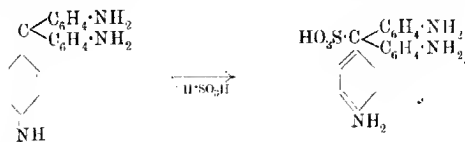
Simple examples of reactions of this type are seen in the formation of the indamines and indophenols by conjoint oxidation of para-diamines or para-aminophenols with amines or phenols. Taking phenylene-blue as typical of these compounds, the reactions occurring may be represented as follows:



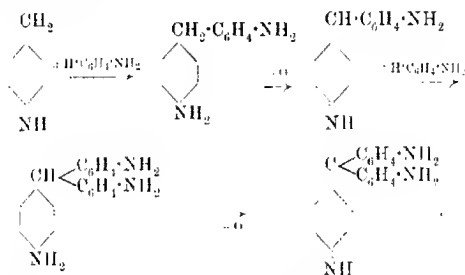
The formation of indamines or indophenols from nitrosoamines or nitrosophenols can also be represented in a similar manner:



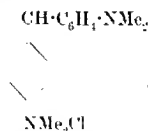
The tendency of the triphenylmethane dyestuffs to form colourless compounds by combination with sulphurous acid, hydrogen cyanide, water, etc., has been represented by Thiele as follows:



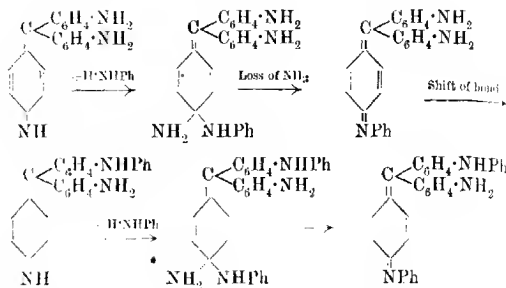
Most of the reactions which lead to dyestuffs of the triphenylmethane group can be better explained as additive processes than by the ordinary method of representation; thus the formation of pararosaniline by oxidation of a mixture of *p*-toluidine and aniline may be represented by assuming that the former is first oxidised to the carboquinonimide which then reacts with aniline in the following manner:



The hydrol and carbonyl chloride syntheses of triphenylmethane dyestuffs may also be regarded in a similar light; thus the extraordinary facility with which tetramethyldiaminobenzhydrol undergoes condensation with a wide range of substances is explained if we attribute these reactions to the additive capacity of the hydrol salt in its quinonoid form:



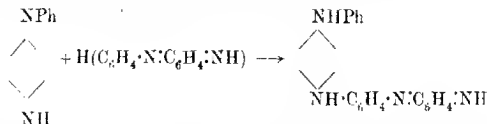
Even the phenylation of rosaniline in the production of aniline blue may be regarded with great probability as a quinonoid reaction, although of a different type from the above.



and so on.

This method of representation accounts for the readiness with which phenylation takes place compared with the ordinary phenylation of amines, and also explains the function of the benzoic acid used. This weak acid preserves a sufficient degree of acidity to determine the elimination of ammonia without retaining the latter in the reacting mixture, so that the reaction can proceed to completion. If hydrochloric acid is used instead, the accumulation of ammonium chloride brings about an equilibrium, through the reversal of the reaction, when only the mono- or di-phenylated stage has been reached.

Recent investigations on aniline-black have demonstrated that the intermediate products of its formation, emeraldine and nigraniline, are complex indamines containing eight aniline residues linked together in the para-position. A study of the formation of these compounds (Willstätter and Moore, *Ber.*, 1907, **40**, 2665; Green and Woodhead, T., 1910, **97**, 2388) makes it very probable that the mechanism of their formation is as follows: The first oxidation product of aniline capable of isolation is the yellow phenylquinonimide of Caro. This substance, under the influence of mineral acids, is at once converted into the blue imide of Willstätter, a reaction which consists in the direct addition of one molecule of the yellow imide to the quinonoid groups of a second:

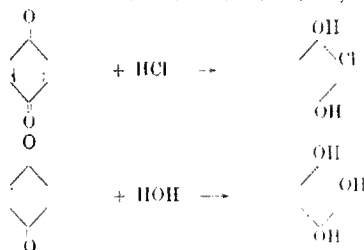


Further oxidation of the blue imide gives the red imide of Willstätter,  $\text{NPh}\cdot\text{C}_6\text{H}_3\cdot\text{N}:\text{C}_6\text{H}_3\cdot\text{N}:\text{C}_6\text{H}_3\cdot\text{NH}$ , and this also under the influence of mineral acids undergoes a similar addition and produces

nigraniline. Or the blue imide may, by addition to the red imide, produce emeraldine, which latter on oxidation gives nigraniline. The tendency to the formation of such complex molecules is thus readily explained.

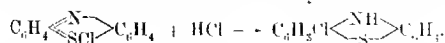
#### Indirect Quinonoid Addition.

Simple examples of indirect quinonoid addition are to be found in the conversion of *p*-benzoquinone into chloro- or hydroxy-quinol by the action of hydrochloric acid or of sodium hydroxide respectively (Barth and Schreder, *Ber.*, 1879, **12**, 417, 503):



An important case in which the latter reaction occurs is the formation of dihydroxyanthraquinone (alizarin) by alkali fusion of anthraquinonemonosulphonic acid or even of anthraquinone itself, and a similar introduction of hydroxyl probably constitutes an intermediate stage in the production of indanthren-blue by the alkaline fusion of 2-aminoanthraquinone. Thiele (*Ber.*, 1898, **31**, 1247; *Annalen*, 1900, **311**, 341) has also found that acetyl derivatives of chloro- or hydroxy-quinol are readily formed from *p*-benzoquinone by the action of zinc chloride or concentrated sulphuric acid respectively in the presence of acetic anhydride. A similar reaction has been described by Schultz (*Ber.*, 1882, **15**, 652), who obtained diacetyldichloroquinol by the action of acetyl chloride on *p*-benzoquinone.

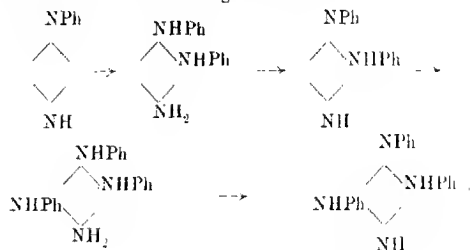
Many analogous cases have been observed amongst ortho-quinonoid dyestuffs; thus Page and Smiles (*T.*, 1910, **97**, 1112) have observed the ready formation of chloro-compounds from phenazothionium salts when heated with hydrochloric acid:



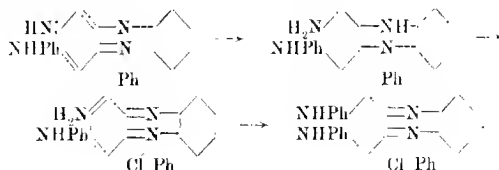
Other simple cases of indirect quinonoid addition are to be found in the formation of *p*-phenylenediaminesulphonic acid, and of the mono-, di-, and tetra-thiosulphonic acids of *p*-phenylenediamine obtained by oxidation of this base in the presence of sulphurous

or thioisniphuric acids (compare Green and Perkin, *T.*, 1907, 83, 1201). Probably similar reactions, giving rise to intermediate chain derivatives, constitute an important factor in the formation of sulphur dyestuffs when *p*-aminophenols and hydroxydiphenylamine derivatives are heated with sodium polysulphide.

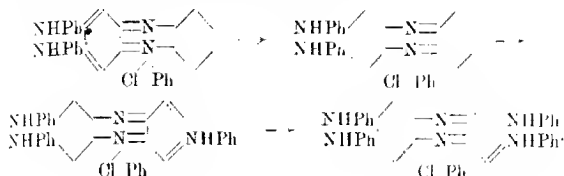
The direct introduction of amino-groups into the nucleus of quinones or quinonoid compounds is known in a large number of cases; thus  $\alpha$ - and  $\beta$ -naphthaquinones, when treated with aniline, are converted into their monoanilino-derivatives,  $C_{10}H_5O_2NHPh$ , whilst *p*-benzoquinone gives dianilino-*p*-benzoquinone and its anilides. Anilino-derivatives of *p*-benzoquinone and of *p*-benzoquinoneanilides are also produced when aniline is subjected to oxidation under neutral or very feebly acid conditions (compare Willstätter and Majima, *Ber.*, 1910, 43, 2588; Majima, *Ber.*, 1911, 44, 229, 3080). These compounds constitute the intermediate stages in the formation of indulines and nigrosines, in which cases the rôle of oxidising agent is fulfilled by the aminoazobenzene or nitrobenzene respectively. Assuming as before that the primary oxidation product of aniline is again the yellow imide of Caro, we may picture the further condensation to occur by alternate addition and reoxidation in the following manner:



All these compounds give rise to indulines on heating with aniline and anilino hydrochloride, the closing of the phenazonium ring being attributable to direct quinonoid addition, in which the amine residue taking part in the reaction is a portion of the quinonoid molecule itself:



By the transference of the quinonoid bonds to the other ring, an occurrence which has been specially studied by Kohnmann (*Ber. 1938, 31, 977*), this ring also becomes capable of indirect addition, and thus a further introduction of amine residues is effected, and bluer shades of induline are produced:



The introduction of amine residues into the benzene or naphthalene nucleus brought about by indirect quinonoid addition has been observed in a large number of cases in the azine, thiazine, and oxazine series. Amongst them may be instanced the conversion of phenylphenazonium chloride into *aposafranine*, of phenylnaphthaphenazonium chloride into *rosinduline*, and of Meldola's blue into substituted derivatives of Nile-blue.

The formation of all dyestuffs belonging to the azine, oxazine, and thiazine series, starting from their respective raw materials, are readily represented by a series of indirect and direct quinonoid additions with intermediate reoxidations (compare Bucherer).

Similar considerations can probably be applied to explain the formation of dyestuffs of other classes; thus the great tendency exhibited in the anthraquinone series to the production of complex ring systems (vat dyestuffs) is possibly attributable to the attraction for hydrogen exerted by the ketonic groups. Even in the azo-class it seems not impossible that the formation of the dyestuff may be preceded by an unstable quinonoid form of the diazonium compound (compare Cain).

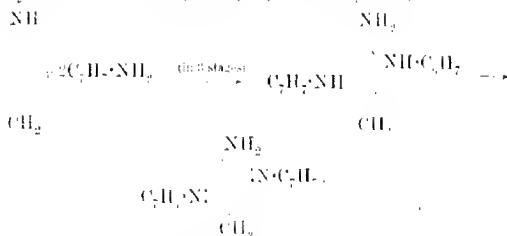
As to the conditions which predispose to direct or indirect quinonoid addition, it may be noted in general with regard to amines, that whilst strongly acid conditions favour direct quinonoid addition (formation of indamines, formation of triphenylmethane dyestuffs, etc.), neutral or weakly acid conditions favour indirect quinonoid addition (formation of anilinoquinones, etc.). In other words, amine salts tend to add *directly*, reacting as  $\text{H}(\text{C}_6\text{H}_4\cdot\text{NH}_2)$ ; free amines *indirectly*, reacting as  $\text{H}(\text{NH}\cdot\text{C}_6\text{H}_4)$ . This is well brought out in the oxidation of aniline under various circumstances, in which it is clearly apparent that the condition of acidity is the determining factor which regulates the ultimate product obtained (see scheme on p. 932). In all cases Caro's yellow imide is probably



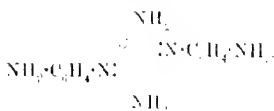


the first product of the reaction, but whilst in acid solution this undergoes direct quinonoid addition, with itself finally giving emeraldine and nigraaniline, in neutral solution it suffers indirect addition with aniline, giving rise to various anilino quinones, which on heating with aniline hydrochloride eventually produce indulines. That the condition of acidity is the determining factor in directing the course of these reactions in one direction or the other is clearly shown by the following simple experiment. If to an alkaline aqueous solution of the yellow imide containing aniline in excess there is added concentrated hydrochloric acid, a blue precipitate of Willstätter's imide is immediately formed. If, on the other hand, a small quantity of dilute hydrochloric acid is first added, a reddish-brown precipitate of an anilino-quinone is produced, which is not further altered by adding concentrated hydrochloric acid a few seconds later.

Exactly analogous to the course of the oxidation of aniline in neutral solution is that of *p*-toluidine and of *p*-phenylenediamine. The former gives Barsilowsky's base, the formation of which probably occurs as follows (Green, T., 1893, 63, 1395):



The production of Bandrowski's base,



from *p*-phenylenediamine may be attributed to an analogous reaction starting from quinoned-imide,

This paper was communicated to the Eighth International Congress of Applied Chemistry, New York, 1912.

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# XCVI.--*Influence of Increase of Initial Temperature on the Explosiveness of Gaseous Mixtures.*

By ALBERT PARKER, B.Sc.

MANY experiments have been carried out by various investigators to determine the lower limits of explosion of combustible gases, such as hydrogen, carbon monoxide, and methane, but these limits are not yet known with any great degree of accuracy, except in the case of methane. This variation in the results obtained is to be explained by the influence of such conditions as size and shape of the containing vessel and the nature and position of the firing agent employed.

Roszkowski (*Zeitsch. physikal. Chem.*, 1891, 7, 185) found that mixtures containing a smaller percentage of combustible gas could be fired in a sphere-shaped vessel better than in a narrow tube. It is also well known that a gaseous mixture contained in a vertical tube is more easily fired by sparking at the bottom than at the top. Roszkowski carried out many experiments on the influence of initial temperature on explosion limits of gases, but since that time very little work has been done on this point.

In the following experiments no attempt has been made to determine the lower limits of a combustible gas at different temperatures when mixed with air or oxygen, but an attempt has been made to obtain a mixture which would not completely explode by sparking at one temperature, and would completely explode when sparked at some other temperature. In this way the effect of change of initial temperature could be ascertained.

Experiments were made with hydrogen, methane, carbon monoxide, and coal gas. The gaseous mixtures were made by mixing measured volumes of the constituent gases in a glass gasometer containing water; consequently, the mixtures were saturated with water-vapour at from 15° to 18°. The gasometer held about 15 litres, which was sufficient to allow many experiments to be made at the ordinary temperature and at 100°. This was essential, as it is very difficult to obtain two mixtures of identical composition, especially when dealing with coal gas mixtures.

The gaseous mixtures were made by first making a mixture of a certain known composition, and then altering it by addition of one or other of the constituent gases until the required mixture was obtained; for example, in the case of mixtures of methane and oxygen, a mixture containing 6.35 per cent. of methane was first made. This was found to explode completely at the ordinary temperature. A calculated quantity of oxygen was then added

so that the gas contained 6.3 per cent. of methane. A further quantity of oxygen was added, altering the composition to 6.25 per cent. of methane, which was found to be the required mixture.

*Apparatus.*—The apparatus consisted of a graduated explosion pipette of 100 c.c. capacity. The sparking platinum points were near to the top, so that the volume above the platinum points was only 1 c.c. A three-way tap allowed the pipette either to be opened to the air or connected to the gasometer containing the mixture to be examined. The pipette was surrounded by a wide glass tube, through which steam could be passed. The volume and pressure of the gas to be fired were controlled by means of a mercury reservoir. A break spark of constant strength was used to fire the gases, and was obtained from a Ruhmkorff coil by screwing the coil up and rapidly breaking the contact by means of the switch. The gas was measured under atmospheric pressure before and after sparking, and the amount of gas burned was calculated from the observed contraction.

Experiments were conducted with the various gaseous mixtures at the ordinary temperature, and at three different pressures. At 100° experiments were made at (1) atmospheric pressure, (2) a pressure equal to that which would have been obtained by heating the gas from the ordinary temperature to 100° at constant volume, and (3) a still higher pressure. In this way the effects of pressure change could also be observed. The progress of the flames produced on sparking was followed after previously darkening the room.

#### *Experiments with Hydrogen.*

For these experiments mixtures of hydrogen with oxygen and with air were used. The hydrogen was prepared from pure zinc and sulphuric acid, and was freed from hydrocarbons by passing through hot potassium permanganate solution. The oxygen was prepared from manganese dioxide and potassium chlorate, and was freed from chlorine by means of sodium hydroxide solution. The results obtained for hydrogen mixtures are given in the following tables. Each result represents the mean value of several experiments.

TABLE I.  
Hydrogen: 8.4, oxygen 21.6 per cent.

Temperature.	Pressure in mm.	Amount burned, Per cent.	OF SEVERAL TESTS.
17°	763	0.57	Flame only travelled a short distance down the tube.
17	1056	0.7	
17	1342	0.76	
160	763	0.80	
160	970	1.1	
160	1361	1.3	

The above results showing the percentage of hydrogen burned are calculated on the total volume of the mixture used.

TABLE II.

Hydrogen=8.7, oxygen=91.3 per cent.

Temperature.	Pressure in atm.	Amount burned. Per cent.	Observations.
17°	766	1.3	Flame part way
17	(1011	1.9	" " "
17	(1011	7.3	" through
17	1335	1.9	" part way
100	766	1.8	" " "
100	( 971	2.1	" " "
100	( 971	8.6	" through
100	(1384	5.3	" part way
100	(1384	8.65	" throughout

TABLE III.

Hydrogen=8.7, air=91.3 per cent.

Temperature.	Pressure in atm.	Amount burned. Per cent.	Observations.
17°	754	1.14	Flame part way
17	974	1.36	
17	1347	1.7	
100	( 754	1.85	" " "
100	( 754	8.45	" throughout
100	( 960	2.1	" part way
100	( 960	8.48	" throughout
100	(1378	3.1	" part way
100	(1378	8.42	" throughout

In some cases in the above results two values are given for the percentage of hydrogen burned under the same conditions of temperature and pressure. This is to show that sometimes on sparking the flame travelled only a short distance, and at other times the flame travelled throughout the mixture. The lower value given is the mean of the results obtained from the experiments in which the flame travelled only a short distance, and the higher value is the mean of those experiments in which the flame travelled throughout.

From the foregoing results for hydrogen mixtures it may be concluded:

(1) When a mixture of hydrogen with oxygen or with air below the lower limit is sparked at an initial temperature of 17° or 100°, increase of initial pressure from one to two atmospheres causes an increase in the amount of hydrogen burned.

(2) Rise of initial temperature increases the amount of hydrogen burned.

(3) Even in those experiments in which the flame has travelled throughout the gas, the combustion of hydrogen is incomplete, and it is more incomplete at the ordinary temperature than at 100°.

(4) It is possible to obtain a mixture of hydrogen with oxygen or with air which will not explode at the ordinary temperature and pressure, but which will explode when heated to 100° at either constant pressure or constant volume.

*Experiments with Carbon Monoxide.*

The carbon monoxide was prepared from sodium formate and sulphuric acid, and was purified from carbon dioxide by means of potassium hydroxide solution. Analysis of the gas showed it to contain 99·8 per cent. of carbon monoxide.

TABLE IV.

Carbon monoxide = 14·5, air = 85·5 per cent.

Temperature.	Pressure in mm.	Amount burned. Per cent.	Observations.
15°	771	0·57	Flame part way
15	1018	0·71	
15	1351	0·86	
100	771	14·3	Flame throughout
100	981	14·5	
100	1270	14·5	

TABLE V.

Carbon monoxide = 15·7, oxygen = 84·3 per cent.

Temperature.	Pressure in mm.	Amount burned. Per cent.	Observations.
15	755	0·26	Flame part way
15	987	1·72	
15	1237	2·0	
100	755	15·6	Flame throughout
100	961	15·7	
100	1337	15·65	

From the results for carbon monoxide mixtures it may be concluded that:

(1) Increase of initial pressure increases the amount of carbon monoxide burned.

(2) Increase of initial temperature increases the amount of carbon monoxide burned.

(3) It is possible to obtain a mixture of carbon monoxide with air or oxygen which will not completely explode at the ordinary temperature and pressure, but which will completely explode after heating to 100° at either constant pressure or constant volume.

(1) It was also found that a 15 per cent. mixture of carbon monoxide and air completely exploded when sparked at the ordinary temperature and pressure, whereas a 15 per cent. mixture of carbon monoxide and oxygen did not completely explode under the same conditions.

*Experiments with Methane.*

The methane was prepared by the action of hot water on pure previously fused aluminium carbide. The evolved gas was purified by passing through an ammoniacal solution of cuprous chloride to remove acetylene, and then through dilute sulphuric acid to remove ammonia. The gas thus prepared was carefully analysed, the hydrogen present being estimated by mixing with oxygen and passing the mixture over palladium-black. Rather more than the calculated quantity of oxygen was added, and the mixture dried by passing through sulphuric acid. The dry gas was passed over palladium-black at 100°, and then through alkaline pyrogallate solution to remove oxygen. Analysis showed the gas to only contain a small quantity of nitrogen as impurity.

TABLE VI.

Methane = 6.0, air = 94.0 per cent.

Temperature.	Pressure in mm.	Amount burned. Per cent.	Observations.
16°	755	0.56	Flame part way
16	988	0.71	
16	1297	0.86	
100	755	6.0	
100	981	5.9	Flame throughout
100	1337	6.0	

TABLE VII.

Methane = 6.25, oxygen = 93.75 per cent.

Temperature.	Pressure in mm.	Amount burned. Per cent.	Observations.
16°	768	0.86	Flame part way
16	1000	1.0	
16	1312	1.15	
100	768	6.30	
100	974	6.20	Flame throughout
100	1337	6.25	

From the above results for methane mixtures it may be concluded that:

(1) Increase of initial temperature or pressure causes an increase in the amount of methane burned.

(2) It is possible to obtain a mixture of methane with air or oxygen which will not completely explode when sparked at the ordinary temperature and pressure, but which will completely explode when sparked after heating to  $100^{\circ}$  at either constant pressure or constant volume.

(3) It was also found that a 6.2 per cent. mixture of methane and air completely exploded when sparked at the ordinary temperature and pressure, whereas a 6.2 per cent. mixture of methane and oxygen did not completely explode under the same conditions.

#### *Experiments with Coal Gas.*

In the experiments with coal gas mixtures the same sample of gas was not used for oxygen as for air mixtures, so that probably the composition of the coal gas differed slightly in the two series.

TABLE VIII.

Coal gas = 9.4, oxygen = 90.6 per cent.

Temperature.	Pressure in mm.	Amount burned, Per cent.	Observations.
$17^{\circ}$	764	1.87	Flame part way
17	1038	2.07	
17	1341	2.23	
100	764	3.0	" " "
100	744	9.4	
100	971	3.1	" throughout
100	971	9.2	" part way
100	1341	9.2	" throughout
100	1341	2.9	" part way
100	1341	9.2	" throughout

TABLE IX.

Coal gas = 8.55, air = 91.45 per cent.

Temperature.	Pressure in mm.	Amount burned, Per cent.	Observations.
17	752	1.2	Flame part way
17	1034	1.7	
17	1336	2.2	
100	752	8.3	" throughout
100	977	8.5	
100	1380	8.5	

In order to be able to calculate the amount of coal gas burned from the observed contraction in volume, it was first necessary to make a richer mixture of coal gas and air of known composition, and observe the contraction in volume after sparking at the ordinary temperature and at  $100^{\circ}$ . The results obtained for coal gas mixtures are very similar to those which were obtained for hydrogen, carbon monoxide, and methane.



*General Conclusions.*

(1) Increase of initial temperature of gaseous mixtures of hydrogen, carbon monoxide, methane, or coal gas with air or oxygen causes an increase in the explosiveness of such mixtures; that is to say, the values of the lower limits of such gases are lowered. This is the effect to be expected, since when the temperature is raised the mixture is brought nearer to its ignition-temperature, and the cooling effect produced by the walls of the containing vessel is decreased.

(2) The effect of increase of initial temperature is much less in the case of hydrogen mixtures than with methane or carbon monoxide mixtures.

(3) Increase of initial pressure also increases the explosiveness of the above gaseous mixtures.

(4) The lower limit of hydrogen is approximately the same when mixed with air as when mixed with oxygen, but the values of the lower limits of carbon monoxide, methane, and coal gas are higher for oxygen mixtures than for air mixtures.

I wish to express my indebtedness to Prof. Dixon for much valuable advice during the course of this work.

UNIVERSITY OF MANCHESTER.

XCVII.—*Allylamine Derivatives.*

By WILHELM GLUUD, Ph.D.

The production of pyrrole from allyl derivatives has been described by Königs (*Ber.*, 1879, **12**, 2344), who passed ethylallylamine over lead oxide at 400–500°. Since then no progress has been effected in this method of preparing pyrrole, and the description of the following compounds may therefore be of interest. The reaction and its application to similar substances will be dealt with in another communication.

The simplest acyl derivative of allylamine is allylformamide, the empirical formula of which differs from that of pyrrole only by one molecule of water:



It seems, however, to have only a slight tendency to pass into pyrrole derivatives, although these can be obtained by heating allylformamide to  $260^{\circ}$ , but the yield was so small that the reaction did not repay further investigation. The high temperature caused the formation of many decomposition products, including carbon monoxide and ammonium carbonate. Dehydrating agents gave no better results.

Allylthiocarbimide on heating with sodium in a sealed tube gave compounds which showed the pyrrole reaction with pine-wood quite distinctly, and a similar result was obtained by passing the vapour of the compound over heated copper, but in both cases the yield was very small owing to the violent character of the reaction. It is a remarkable fact, however, that small quantities of pyrrole compounds are formed during the preparation of allylformamide from allylthiocarbimide and formic acid.

It occurred to me that better results might be obtained by using allyloxamic acid, an expectation which has been satisfactorily confirmed, as this substance was found to be an excellent material for the production of pyrrole derivatives. For this purpose it was necessary to find an easy way of preparing it. An attempt was made to obtain it by a method analogous to that used by Clayton (*Ber.*, 1895, 28, 1666) in the preparation of allylformamide, namely, from oxalic acid and allylthiocarbimide, but the products of the reaction are complicated and difficult to separate, being for the most part allylamine oxalates, besides the allylamine salt of allyloxamic acid, and some compounds containing sulphur. The latter were not investigated, as they were of no use for the purpose of this research, but possibly they may be of interest as intermediate products, as they readily evolve carbonyl sulphide, and may therefore be assumed to contain this substance only loosely combined. A better method was to prepare the ethyl ester of allyloxamic acid from allylamine and ethyl oxalate, and then to hydrolyse the ester.

#### EXPERIMENTAL.

##### *Allylformamide*, $\text{CH}_2\text{CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CHO}$ .

This substance was previously prepared by Clayton (*Ber.*, 1895, 28, 1666), but as no details of the yield are given, some improvements may be noted which ensure a rapid preparation of any quantity of the compound. If anhydrous formic acid is used, the reaction takes much less time, and can be carried out on a water-bath, and the oil need not be distilled under diminished pressure.

Allylthiocarbimide (102 grams) and anhydrous formic acid (56 grams) are heated under reflux on the water-bath, the condenser

being connected to a gas wash-bottle filled with water. The evolution of gas begins at once, but after about an hour the reaction suddenly becomes violent, and should be moderated by slightly lowering the temperature. When the liquid stops boiling the reaction is completed by heating for half an hour on the water-bath. The liquid is then distilled; much carbonyl sulphide is evolved below  $190^{\circ}$ , and the allylformamide passes over at  $213-218^{\circ}$ , the yield being about 70 per cent. of the theoretical. The residue in the flask gave the pyrrole reaction with pine-wood. In another experiment, from 150 grams of allylthiocarbamide 91 grams of allylformamide were obtained, which boiled at  $215-216^{\circ}$ . It is an oily liquid with an unpleasant odour, readily soluble in water, ether, or alcohol. When prepared in this way, it is pure enough for most purposes, but can be purified by extraction with light petroleum or by redistillation over charcoal; the compound then still contains traces of sulphur.

If allylformamide, however, is distilled over phosphoric oxide or zinc chloride, a small quantity of oil passes over about  $120-140^{\circ}$ . This oil is lighter than water, and does not mix with it; it gives the pyrrole reaction distinctly. On heating allylformamide in a sealed tube for several hours, decomposition begins about  $200^{\circ}$ . There is a high pressure in the tubes, due to carbon monoxide, and a small quantity of a pyrrole derivative of high boiling point is formed, along with resinous products and ammonium carbonate. Similar results were obtained when allylacetamide was used.

*Diallyloxamide*,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ .

This compound was prepared by Wallach and Stricker (*Ber.*, 1880, **13**, 513), but no accurate description of the preparation, properties, or details of analysis are given in their paper. Allylamine (3.8 grams) dissolved in 25 c.c. of ether is mixed with freshly distilled ethyl oxalate (3.5 grams) dissolved in 25 c.c. of ether, and the mixture cooled to  $0^{\circ}$ . After several hours the crystals formed (3.5 grams) are collected and recrystallised from acetone. Analysis of the compound, dried in a desiccator, showed that it was quite pure, the yield being about 87 per cent. of the theoretical:

0.1631 gave 0.3412  $\text{CO}_2$  and 0.1020  $\text{H}_2\text{O}$ .  $\text{C}=57.05$ ;  $\text{H}=7.00$ .

0.1700 " 23.8 c.c.  $\text{N}_2$  at  $16^{\circ}$  and 768 mm.  $\text{N}=16.51$ .

$\text{C}_6\text{H}_{12}\text{O}_4\text{N}_2$  requires  $\text{C}=57.10$ ;  $\text{H}=7.19$ ;  $\text{N}=16.67$  per cent.

The compound crystallises in long, narrow plates, fairly soluble in hot alcohol, chloroform, benzene, and excess of hot water or ether. It is readily soluble in warm dilute acetic acid, and addition of calcium chloride and sodium acetate to the solution

produces no precipitation of oxalate even on boiling for a short time.

The aqueous solution rapidly decolorises bromine water. When boiled with alkalis, allylamine is evolved.

*Allyloxamic Acid*,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ .

In order to obtain this compound, it is first necessary to prepare the *ethyl* ester,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ . This is done by mixing 100 grams of ethyl oxalate in 100 c.c. of ether with 37 grams of allylamine in 60 c.c. of ether and cooling to  $0^\circ$ . After an hour, the ether is evaporated off, and the residue which contains crystals is shaken with light petroleum. The solid remains suspended in the ether, and the ethyl allyloxamate which forms the lower layer is easily separated. On distillation, a small fraction passes over below  $100^\circ$ , then the temperature rises rapidly, and at  $252^\circ$  the ester (66 grams) distils over, the yield being 65 per cent. of the theoretical. It still, however, contains a small quantity of diallyloxamide, which partly separates on cooling. If the whole is hydrolysed this impurity can be completely removed.

The ester is a pale yellow liquid with an unpleasant, garlic odour. It is heavier than water, and readily soluble in the usual organic solvents or in excess of hot water, from which it separates on cooling. The aqueous solution decolorises bromine-water immediately.

In the following experiments it was unnecessary to use the pure product. The ester (2.3 grams) is shaken with 15 c.c. of *N*-sodium hydroxide until, after half an hour, the garlic odour has disappeared. Then 15 c.c. of *N*-hydrochloric acid are added, when crystals of diallyloxamide separate out. These are collected, and the filtrate is evaporated to dryness. The residue is extracted with ether and the solution evaporated, leaving a syrupy mass, which, on mixing with light petroleum, soon becomes crystalline (1.3 grams). The crystals can be purified by recrystallisation from a very small quantity of benzene and then from chloroform, from which allyloxamic acid (0.85 gram) separates in silky, square plates, which melt at  $97-98^\circ$ , forming a colourless liquid. They are very soluble in water, alcohol, or acetone, readily so in ether, hot chloroform or benzene, and sparingly soluble in hot light petroleum. From the last three solvents the substance crystallises on cooling the solution. The aqueous solution decolorises bromine-water at once. The substance, after being left in a desiccator, was analysed:

0.2093 gave 0.3563  $\text{CO}_2$  and 0.1032  $\text{H}_2\text{O}$ .  $\text{C} = 46.43$ ;  $\text{H} = 5.52$ .

0.2021 " 18.8 c.c.  $\text{N}_2$  at  $18^\circ$  and 760 mm.  $\text{N} = 10.86$ .

$\text{C}_4\text{H}_5\text{O}_3\text{N}$  requires  $\text{C} = 46.49$ ;  $\text{H} = 5.47$ ;  $\text{N} = 10.85$  per cent.

The *calcium* salt is prepared by mixing the crude ethyl ester (50 grams) with 160 c.c. of 2*N*-sodium hydroxide and cooling to 0°. When all the oil has disappeared, the liquid is filtered, and a solution of anhydrous calcium chloride (20 grams in 50 c.c. of water) is added to the filtrate. On cooling to 0° the calcium salt separates in crystals, which are collected and dried on a water-bath (40.5 grams), the yield being about 80 per cent. of the theoretical. They can be redissolved in about twenty times their volume of boiling water, and the solution cleared with charcoal. From this solution the salt separates in characteristic, narrow, compact prisms, which acquire a syrupy consistency about 160°. Analysis shows that the air-dried crystals contain two molecules of water:

0.2002 g at 100° over phosphoric acid under 10–12 mm. pressure gave 0.0215 H<sub>2</sub>O. H<sub>2</sub>O = 10.74.

C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>N<sub>2</sub>Ca·2H<sub>2</sub>O requires H<sub>2</sub>O = 10.84 per cent.

0.1787 g gave 0.0340 CaO. Ca = 13.60.

C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>N<sub>2</sub>Ca requires Ca = 13.53 per cent.

The salt, when heated alone, or with lime, or equivalent substances, easily yields a yellow oil, which does not mix with water, resinifies with acids, and gives the pyrrole reaction.

The *potassium* salt is prepared by boiling the aqueous solution of the calcium salt for some minutes with the required quantity of anhydrous potassium hydroxide. The solution is filtered and evaporated on a water-bath, leaving a waxy mass. This is mixed with alcohol, and becomes instantly solid. One gram of this solid is dissolved in a mixture of 20 c.c. of alcohol and 0.5 c.c. of water, from which solution 0.7 gram of the salt crystallises in thin plates. The air-dried salt contains no water of crystallisation, as it loses practically no weight when dried at 100° over phosphoric acid at 10–12 mm. pressure. When heated to 230° it forms a syrupy liquid, which decomposes at a higher temperature, giving oily distillates, which contain pyrrole derivatives.

#### *Action of Oxalic Acid on Allylthiocarbimide.*

Crystallised oxalic acid (30 grams) and allylthiocarbimide (30 grams) were heated under reflux for five hours at 125°. The action was not then complete, as the evolution of gas still continued. The product, which solidified on cooling, was washed with light petroleum to remove any unchanged allylthiocarbimide, and 23 grams were crystallised from alcohol, from which transparent prisms separated, melting at 135–136°, readily soluble in hot

\* Air dried.

† Anhydrous.

water or alcohol, but practically insoluble in most organic solvents. It was dried in a vacuum desiccator, and then analysed:

(b) 1943 gave 0.2905  $\text{CO}_2$  and 0.1105  $\text{H}_2\text{O}$ .  $\text{C}=40.78$ ;  $\text{H}=6.36$ .

$\text{C}_5\text{H}_9\text{O}_4\text{N}$  requires  $\text{C}=40.80$ ;  $\text{H}=6.17$  per cent.

The product is therefore *allylamine hydrogen oxalate*. When heated above its melting point much gas is evolved, and a colourless residue left, which does not give the pyrrole reaction. It can also be prepared by mixing 1.2 grams of allylamine with a solution of 2 grams of oxalic acid in alcohol or acetone in the cold.

In another experiment a mixture of allylthiocarbimide (52 c.c.) and crystallised oxalic acid (77 grams) was heated on a water-bath for about twenty-five hours until no further evolution of gas was observed, and the odour of allylthiocarbimide had disappeared. The product was a clear liquid, which on cooling solidified to a waxy substance, consisting of an oil (24 grams) and a waxy solid (7.5 grams). The oil was evaporated on a water-bath, and the partly crystalline residue shaken with acetone, when allylamine oxalate (7.5 grams) separated out. The wax-like solid was also shaken with acetone, in which the greater part dissolved, leaving 20 grams of fine crystals melting at  $130-134^\circ$ . (Allylamine hydrogen oxalate melts at  $135-136^\circ$ .) The acetone solution was evaporated in a vacuum, yielding 21 grams of an unpleasant-smelling oil, which solidified on cooling, and appeared to be a mixture of various sulphur compounds, as on heating it gave off much carbonyl sulphide. The production of allylamine oxalate shows that if the reaction is allowed to be completed there is still not sufficient oxalic acid in spite of the excess used.

A mixture of anhydrous oxalic acid (55 grams) and allylthiocarbimide (50 grams) when heated for eighteen hours on a water-bath yielded 55 grams of crystals, more than 60 per cent. of which consisted of allylamine hydrogen oxalate, so that in this experiment also oxamic allyl acid could only have been formed in small quantity.

One experiment may be described, showing the course of this reaction in aqueous solution. Crystallised oxalic acid (70 grams), 50 grams of allylthiocarbimide, and 100 c.c. of water were boiled under reflux for thirty six hours, the reaction being then complete. The liquid was evaporated on a water-bath until the aqueous layer acquired a syrupy consistency, when it was mixed with twice its volume of alcohol, and the crystals of allylamine oxalate (24 grams) formed were collected. The mother liquor was evaporated to dryness and the residue dissolved in alcohol, when a further separation of the oxalate (6 grams) took place. The filtrate was mixed with ether, and kept in ice for some hours. The crystals then

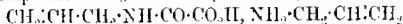
formed (8.5 grams) were removed from the solution, which on evaporation left an oil, which was not further investigated. The crystalline product was recrystallised from a very small quantity of hot chloroform and again from 50 c.c. of acetone; 3 grams of this product were again recrystallised from 75 c.c. of acetone, from which thin, transparent plates (2 grams) separated, melting at 111–112°. These were dried at 100° and analysed:

0.1622 gave 0.3014  $\text{CO}_2$  and 0.1091  $\text{H}_2\text{O}$ .  $\text{C}=51.18$ ;  $\text{H}=7.53$

0.1588 „ 19.8 c.c.  $\text{N}_2$  at 17° and 772 mm.  $\text{N}=14.73$ .

$\text{C}_5\text{H}_{14}\text{O}_3\text{N}_2$  requires  $\text{C}=51.58$ ;  $\text{H}=7.58$ ;  $\text{N}=15.05$  per cent.

This compound is *allylamine allyloxamate*,



It can also be prepared from the corresponding calcium salt. One gram of allylamine was added to 3 grams of the calcium salt dissolved in 75 c.c. of hot water, and the calcium precipitated with carbon dioxide. The hot solution was filtered, evaporated in a vacuum, and the residue dissolved in hot acetone. On cooling, 2.4 grams of crystals separated, which were identical with the above allylamine salt. It is extremely soluble in water or hot alcohol, very sparingly so in ether or benzene. The aqueous solution is neutral, decolorises bromine water instantly, and on addition of calcium chloride yields the corresponding very characteristic calcium salt.

*Allylamine oxalate*, as obtained in the above experiment, can be purified by crystallisation from 95 per cent. alcohol. Three grams of the purified product were dissolved in 100 c.c. of hot 97.5 per cent. alcohol, from which solution, on gradually cooling, small, compact prisms separated out on the sides of the flask. The liquid was then decanted and slowly cooled. This product was dried in a vacuum desiccator and analysed:

0.1522 gave 0.2638  $\text{CO}_2$  and 0.1027  $\text{H}_2\text{O}$ .  $\text{C}=47.27$ ;  $\text{H}=7.55$ .

0.1300 „ 15.2 c.c.  $\text{N}_2$  at 18° and 770 mm.  $\text{N}=13.73$ .

$\text{C}_5\text{H}_{10}\text{O}_4\text{N}_2$  requires  $\text{C}=47.03$ ;  $\text{H}=7.90$ ;  $\text{N}=13.73$  per cent.

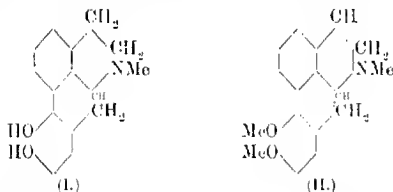
It melts and decomposes at 181°, and is very soluble in water, but practically insoluble in organic solvents. It can also be prepared by mixing 2.5 grams of oxalic acid and 2.5 grams of allylamine in acetone solution at 0°. The crystals formed are collected and recrystallised from 97 per cent. alcohol.

DAVEY FARADAY LABORATORY.

XVIII.—*Experiments on the Synthesis of apoMorphine.*

By FRANCIS WILLIAM KAY and AMÉ PICTET.

THE base, *apomorphine*,  $C_{17}H_{17}O_2N$ , which, as is well known, forms one of the products obtained by the dehydration of morphine,  $C_{17}H_{19}O_3N$ , has been studied by a number of investigators, with a view to elucidate its chemical constitution. Amongst these, Pschorr and his pupils must be placed in the first rank, for it is due to their exhaustive investigations (*Ber.*, 1902, **35**, 4377; 1907, **40**, 1984, 1995, 1998) that an insight has been obtained into the constitution of this alkaloid. As a result of their researches, Pschorr and his pupils deduce formula I as the most probable expression of the structure of *apomorphine*:



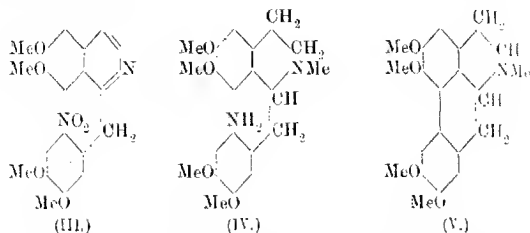
This formula bears a considerable resemblance to that of laudanose (II), as can be seen on comparing the two.

According to Pschorr, the nucleus in *apomorphine* differs from that in laudanose only by containing a bond which unites the two benzene rings, and *apomorphine* must thus be considered a derivative of phenanthrene. We have proposed experimentally to verify this hypothesis of Pschorr by attempting a synthesis of *apomorphine*, starting from a compound already containing the nucleus of laudanose, and then effecting therein the supplementary link in question. Two analogous researches which have already been made and serve as a guide in our present work are due to Pschorr and Gadamier.

Pschorr (*Ber.*, 1901, **37**, 1926) has attempted to transform papaverine into a derivative of phenanthrene. With this object in view he first proved that the nitropapaverine, obtained by Hesse (*Laudan. Suppl.*, 1872, **8**, 292) by treating papaverine with nitric acid, possesses formula III. He prepared its methochloride, and then by reducing the latter with tin and hydrochloric acid, he obtained aminolaudanose (IV). Apparently, it only remained to diazotise the latter and to treat the product with copper powder, according to the well-known method of Pschorr for synthesising the



derivatives of phenanthrene, in order to obtain a phenanthrenolaudanosine (V):



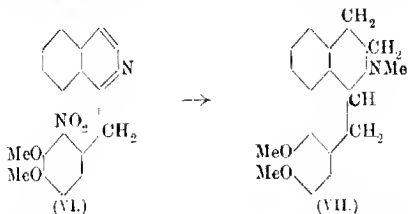
Unfortunately, Pschorr was only able to obtain this last base in the form of a non-crystallisable syrup, and to characterise and analyse it in combination with methyl iodide, that is, as the corresponding methiodide, which crystallises in prisms melting at 215°.

Seven years later Gadamer (*Arch. Pharm.*, 1911, **249**, 680), having repeated this work, showed that the so-called methiodide of phenanthrenolaudanosine, described by Pschorr, was nothing more nor less than the methiodide of racemic laudanosine. The operation of diazotisation, as carried out by Pschorr, had thus merely resulted in eliminating the amino-group of the aminolaudanosine, without closing the phenanthrolic nucleus. By proceeding in a slightly different manner, although still using the same method, Gadamer succeeded in effecting this closure, and obtained in this way the true phenanthrenolaudanosine (V) in the free state and pure (m. p. 137—139°). The latter being inactive to polarised light, whilst from its constitution it should be a racemic substance, Gadamer endeavoured to resolve it into its two optical antipodes. He succeeded in doing so by means of tartaric acid, and was thus able to prove that the dextro-modification (m. p. 119—120°) was identical with glaucine, an alkaloid which has been extracted from *Glaucium luteum* and *Corydalis cava*. In this way he realised the first synthesis of a natural alkaloid of the phenanthrene series.

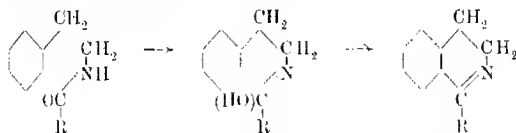
A precisely similar process appeared to offer a means of synthesising apomorphine, which is very closely related to glaucine from a constitutional point of view. It would suffice as the starting point to take nitroveratrylisoquinoline (VI), unknown at present, instead of nitropapaverine (III). By means of the same reactions as used by Pschorr and by Gadamer, it ought to lead to the dimethyl ether of apomorphine (VII).

Our first endeavours were directed to preparing this base (VII) or one of its derivatives hydrogenated in the pyridine nucleus. Although the experiments in this direction have proved abortive,

the authors consider them sufficiently interesting to justify publication. Of all the methods which have been suggested for building



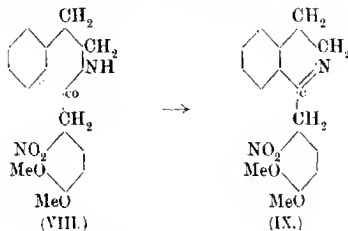
up derivatives of *isoquinoline*, those proposed by the present authors in previous publications (*Ber.*, 1909, **42**, 1973; 1910, **43**, 2384; 1911, **44**, 2030) have the advantage of being comparatively simple, require compounds which are of ready access as the starting point, and give, in addition, remarkably good yields without any harmful by-products. Before commencing the present investigation, we devoted a considerable amount of work to improving and modifying a reaction discovered by Bischler and Napieralski, in such a way as to render it capable of being used in synthesising the *isoquinoline* alkaloids. Briefly stated, our method is as follows. The acyl derivatives of  $\beta$ -phenylethylamine, on boiling with phosphoric oxide in solution in toluene or xylene, lose a molecule of water, and are thereby converted into derivatives of dihydro*isoquinoline*; a reaction which will be readily understood when one writes the substituted amide in its tautomeric enolic form:



A superficial consideration of the formula of the 2-nitro-3:4-dimethoxybenzyl*isoquinoline*, by means of which we had proposed to synthesise dimethyl*apomorphine*, will immediately indicate that we must devise some method of preparing 2-nitrohomoveratroyl- $\beta$ -phenylethylamine, which, when submitted to dehydration under the conditions mentioned above, would undergo cyclisation with the formation of the dihydro-derivative of the required base; so that, for the moment, the whole problem amounts to the synthesis of 2-nitrohomoveratric acid and its condensation with  $\beta$ -phenylethylamine.

Thus far we encountered no great difficulty, but when we came to the conversion of the corresponding amide into the nitroamine,

we were astonished to find that, although dehydration had taken place, there was no trace of a basic substance produced, as would be expected from the following reaction:

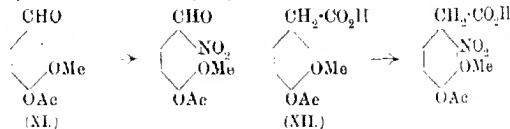


Instead of the latter substance we had obtained an isomeride, derived certainly from 2-nitrohomoveratroyl- $\beta$ -phenylethylamine by the loss of a molecule of water, but without cyclisation. This dehydro-compound yields, indeed,  $\beta$ -phenylethylamine on reduction and saponification. It is somewhat difficult to make a conjecture as to its constitutional formula. The only one which appears to us to satisfy these conditions, but which it must be admitted is far from proved, is  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}:\text{C}:\text{CH}\cdot\text{C}_6\text{H}_4(\text{OMe})_2\cdot\text{NO}_2$  (X).

The failure to effect this cyclisation of 2-nitrohomoveratroyl- $\beta$ -phenylethylamine is evidently due to the presence of the nitro-group. It must be recognised, in our opinion, that this group renders the hydrogen atoms of the neighbouring  $\text{CH}_2$ -group much more mobile, and in such a way that it is one of these atoms- and not the atom of hydrogen in the  $\alpha$ -position in the other benzene ring—which participates in the formation of the molecule of water eliminated in the presence of the phosphoric oxide.

The obstacle presented by the peculiar behaviour of  $\alpha$ -nitrohomoveratroyl- $\beta$ -phenylethylamine has arrested, for the moment, the progress of our research on the synthesis of *apomorphine*, but we are continuing the subject by attacking the problem in another direction.

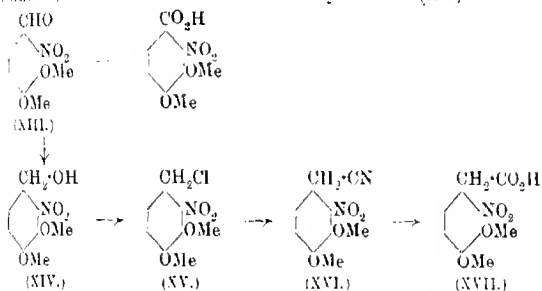
The preparation of the 2-nitrohomoveratric acid required for this synthesis proved to be much more difficult than one would have anticipated. Our first experiments were directed to the nitration of acetylhomovanillic acid, but failed to yield the acid required. Acetylhomovanillic acid (XII) would be expected, from analogy



to acetylvanillin (XI)—which gives 2-nitrovanillin when treated with nitric acid under suitable conditions—to yield the corresponding 2-nitro-acid when nitrated in the same way:

Despite the most varied experimental conditions, it was found impossible to nitrate acetylhomovanillic acid in such a way as to obtain the 2-nitro-acid, and usually either a dinitro-acid probably 1,6-dinitrohomovanillic acid—was produced, or the side-chain was oxidised to carboxyl, leading thus to vanillic acid and its nitro-derivatives, which were quite useless for our purpose.

The method which finally proved successful is somewhat indirect, and has as its starting point 2-nitroveratraldehyde (XIII), which was first obtained by Pschorr. On treating this aldehyde with concentrated potassium hydroxide, it undergoes the Cannizzaro reaction, and is transformed into a mixture of 2-nitroveratryl alcohol (XIV) and 2-nitroveratric acid. The succeeding reactions are quite simple, and need only be mentioned very briefly. On treating the nitro-alcohol with phosphorus pentachloride in benzene solution, it is converted into 2-nitroveratryl chloride (XV):



which yields 2-nitrohomoveratronitrile (XVI) on boiling with alcoholic potassium cyanide. The hydrolysis of this nitrile presented considerable difficulty at first, but finally, on applying Pinner's imino-ether method, it was smoothly converted into 2-nitrohomoveratric acid (XVII).

#### EXPERIMENTAL.

##### *Preparation of 2-Nitroveratryl Alcohol (XIV) from the corresponding Aldehyde by Cannizzaro's Reaction.*

This preparation is based on the well-known fact that the aromatic aldehydes undergo a peculiar transformation when they are treated with concentrated alkali hydroxide solution; benzaldehyde, for example, is converted into a mixture of benzyl alcohol

and potassium benzoate when shaken with concentrated aqueous potassium hydroxide. Under the same experimental conditions, the nitro-aldehydes behave in precisely the same way, and the reaction, which is a very smooth one, furnishes an excellent yield of the corresponding alcohol and acid. 2-Nitroveratraldehyde, which was prepared in quantity by the method described by Pschorr (*Ber.*, 1899, **32**, 3405), can be applied in the same manner, and is converted with remarkable ease into the required alcohol, 2-nitrovanillic acid being naturally obtained as a by-product at the same time.

To 10 grams of 2-nitroveratraldehyde, which are melted in a strong flask, is added a solution of 10 grams of potassium hydroxide in 10 c.c. of water and 10 c.c. of alcohol, and finally thoroughly mixed by vigorous shaking, and occasionally warmed gently on the water-bath. Shortly after the beginning of the reaction, the potassium salt of 2-nitrovanillic acid begins to separate out in glistening leaflets, and the mixture soon solidifies to a thick paste. After twenty-four hours' treatment, accompanied by vigorous shaking, we assumed that the conversion of the aldehyde into alcohol and acid was complete, and then covered the crystalline magna with a fair amount of ether, extracted as much of the nitro-alcohol as possible by agitating for some time, and finally gradually added, with constant shaking, sufficient anhydrous sodium carbonate to bind practically all the water present. In this way a semi-solid, fine-grained mixture of salts is obtained, which is readily exhausted with ether, five extractions being, as a rule, sufficient completely to remove all the adherent alcohol. Traces of unchanged nitro-aldehyde are now removed from the ethereal solution by washing it once with a concentrated sodium hydrogen sulphite solution and then with aqueous sodium carbonate, after which it is dried over freshly ignited sodium sulphate, and finally fractionated on the water-bath, whilst the last traces of alcohol and ether are removed from the residual oil by connecting the vessel with the vacuum pump. After a short time, the viscid, oily residue solidifies to a hard, crystalline cake, which is then spread on porous earthenware to remove liquid impurities. The dry nitro-alcohol is now dissolved in ether, precipitated with light petroleum, and the oil, which separates, dissolved again in a mixture of light petroleum and ether, whilst the impurities remain behind as a resin. The clear filtrate is now treated while hot with light petroleum until a milkiness begins to form, and then allowed to cool. In this way, 2-nitroveratryl alcohol is obtained in slender, yellow needles, which are collected and washed with light petroleum. On allowing the mother liquors to evaporate spontaneously, large, pale yellow,

pointed needles are formed. This alcohol was obtained pure by recrystallising once more from the same solvent mixture:

0.1444 gave 0.2694  $\text{CO}_2$  and 0.0647  $\text{H}_2\text{O}$ .  $\text{C} = 50.88$ ;  $\text{H} = 5.01$ .

0.1967 „ 11.7 c.c.  $\text{N}_2$  at  $21^\circ$  and 731 mm.  $\text{N} = 6.54$ .

$\text{C}_9\text{H}_{11}\text{O}_5\text{N}$  requires  $\text{C} = 50.68$ ;  $\text{H} = 5.21$ ;  $\text{N} = 6.57$  per cent.

The nitro-alcohol melts at  $68-69^\circ$ , and dissolves freely in practically all the usual organic solvents, with the exception of light petroleum, in which it is very sparingly soluble even at the boiling point.

### 2 Nitroveratryl Chloride (XV).

The displacement of the hydroxyl group by chlorine in the alcohol described above is effected by means of phosphorus pentachloride, as the action of hydrogen chloride failed to lead to a satisfactory result.

Two grams of 2-nitroveratryl alcohol are dissolved in 10 c.c. of dry benzene, the solution cooled in ice-water, and gradually treated with 2.1 grams of finely pulverised phosphorus pentachloride, the flask being shaken during the whole of the addition. The phosphorus pentachloride gradually passes into solution, and a little hydrogen chloride is evolved towards the end of the reaction. After remaining for an hour at  $0^\circ$ , the solution, which has meanwhile become paler in colour, is evaporated at  $100^\circ$  in a vacuum in order to remove the phosphoryl chloride, and a viscid, oily residue is obtained, which frequently crystallises directly in the distillation flask, especially if the phosphoryl chloride has been completely removed by dissolving the oil in benzene and evaporating to dryness in a high vacuum. The oily chloride is now dissolved in benzene, filtered, and the clear filtrate diluted with ten times its volume of light petroleum, which causes the precipitation of a little resinous matter—an impurity—which cannot be redissolved by warming the solution. The clear supernatant liquid is decanted hot from the oil, and on cooling deposits a trace of oily impurity, which can be removed by filtration. The filtrate, on complete evaporation on the water bath, yields a viscid oil, which crystallises to a solid cake on keeping for a short time, especially after being seeded with a crystal of the solid chloride. The somewhat impure solid obtained in this way is purified by solution in a little acetone and slow spontaneous evaporation in the air. The crystalline crusts which form are carefully removed, spread in a thin layer on porous porcelain, and washed with a few drops of acetone. For analysis, the white mass is ground to a fine powder and dried over sulphuric acid in a vacuum desiccator. The yield amounts to practically the original weight:

0.2030 gave 0.1228 AgCl.  $\text{Cl} = 14.96$ .

$\text{C}_{10}\text{H}_{10}\text{O}_4\text{NCl}$  requires  $\text{Cl} = 15.30$  per cent.

*2-Nitroveratryl chloride* melts at  $58-59^\circ$ , and crystallises in yellow, waxy leaflets.

*2-Nitrohomoveratronic nitrile (XVI).*

Potassium cyanide (12 grams) is dissolved in 20 c.c. of boiling water and mixed with a solution of 23 grams of 2-nitroveratryl chloride in 250 c.c. of 96 per cent. alcohol, which precipitates some of the cyanide from solution. The mixture is now heated by immersion in a briskly boiling water-bath, and in the course of about two hours sodium chloride begins to separate out, the amount increasing as the reaction proceeds. In about four to six hours the transformation of the chloride into the nitrile is complete, after which the hot alcoholic solution is poured directly into 1250 c.c. of water, seeded with a crystal of the nitrile, and allowed to remain for some time, which causes the nitrile to separate in yellow, felted needles, along with some resin, which can readily be separated mechanically. The crystalline deposit is collected, spread on a porous plate, and finally dried over sulphuric acid in a vacuum. The yield of crude nitrile amounts to 85 per cent. of the theoretical. The purification of the crude nitrile is best effected by boiling it with 5 litres of water, filtering from undissolved oil, and allowing the clear filtrate to cool slowly, when the nitrile separates out, oily at first, but soon crystallises to a mass of long, hair-like needles, which are slightly coloured, and not quite pure because they melt indefinitely between  $60^\circ$  and  $75^\circ$ . The final purification can best be achieved by dissolving the recrystallised material in 40 volumes of methyl alcohol, and then diluting with hot water until a precipitate begins to form. On cooling, the solution deposits at first an oily suspension, which is removed, whilst the residual nitrile in the clear filtrate separates out only very slowly in the cold, and then quite pure, in slender, colourless needles, which are collected and dried over sulphuric acid in a vacuum desiccator:

0.1462 gave 16.9 c.c.  $\text{N}_2$  at  $21^\circ$  and 733 mm.  $\text{N} = 12.77$ .

$\text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_2$  requires  $\text{N} = 12.62$  per cent.

The nitrile melts at  $68-69^\circ$ , and is readily soluble in the usual organic solvents. It is practically insoluble in cold water, but is appreciably soluble in the hot solvent.

*Hydrolysis of 2-Nitrohomoveratronic nitrile: 2-Nitrohomoveratric Acid (XVII).*

Preliminary experiments with potassium hydroxide in aqueous and alcoholic solutions showed that this reagent was entirely unsuited for this saponification, as it only led to the formation of red, uncrystallisable syrups, this being probably due to the presence of the nitro-group. We subsequently found that the nitrile was most conveniently hydrolysed—indirectly, of course—by Pinner's method (*Ber.*, 1883, **16**, 352, 1663; 1884, **17**, 182, 184, 2002; 1892, **25**, 1434; 1895, **28**, 473), an excellent yield of pure acid being readily obtained even from the crude nitrile.

To this end 11 grams (1 mol.) of the nitrile, dissolved in 150 c.c. of absolute ether, are mixed with 8 c.c. (3 mols.) of absolute methyl alcohol, and the solution then saturated at 0° with dry hydrogen chloride. The hydrochloride of the imino-ether frequently separates out of solution during the passage of the hydrogen chloride, and in those cases where it does not, crystallisation usually takes place after a short time, the compound separating in slender, almost colourless needles. The formation of the hydrochloride is complete in a few hours, after which the voluminous, crystalline mass is quickly filtered, washed with dry ether, and finally dried over solid potassium hydroxide in a vacuum desiccator. The yield of imino-ether, starting from crude nitrile, only amounts to 65–75 per cent. of the theoretical, but as only the nitrile can enter into this reaction, whilst the impurities remain dissolved in the ether, this yield is fairly satisfactory, and the method essentially facilitates the preparation of the free acid in a pure state.

The *imino-ether hydrochloride* prepared in this way forms light, colourless needles, which are fairly readily soluble in water, but at the same time it undergoes hydrolytic fission with the formation of ammonium chloride and methyl 2-nitrohomoveratrate, which separates out as an oil.

The direct conversion of the hydrochloride into the free acid is best effected by dissolving it (10 grams) in twenty-five times its weight of water, when a pale yellow, faintly opalescent solution is obtained, which rapidly becomes cloudy owing to the spontaneous separation of the methyl ester. This formation of the methyl ester of the acid is brought to completion by warming the solution for half an hour on the water-bath, after which 40 c.c. of concentrated hydrochloric acid are added, and the boiling continued over a free flame under reflux. In this way the ester which is first formed is saponified and gradually passes into solution in the course of half an hour, whilst complete hydrolysis usually demands two hours. The solution is filtered hot from traces of resin and allowed



to cool, when the acid is obtained in large, yellow leaflets, which can be readily purified by recrystallising once from 40 parts of boiling water. For analysis, the substance is dried at  $120^{\circ}$  until constant in weight, a certain amount of moisture being driven off in the process:

0.1758 gave 0.3204  $\text{CO}_2$  and 0.0707  $\text{H}_2\text{O}$ .  $\text{C}=49.71$ ;  $\text{H}=4.5$ .

0.1804 „ 10.2 c.c.  $\text{N}_2$  at  $22^{\circ}$  and 727 mm.  $\text{N}=6.15$ .

$\text{C}_{10}\text{H}_{11}\text{O}_6\text{N}$  requires  $\text{C}=49.77$ ;  $\text{H}=4.60$ ;  $\text{N}=5.89$  per cent.

The pure acid sinters towards  $143^{\circ}$ , and melts sharply at  $146^{\circ}$ . It dissolves more or less readily in the common organic solvents, and is very sparingly soluble in cold water, but dissolves appreciably in the hot solvent.

#### 2-Nitrohomoveratroyl- $\beta$ -phenylethylamine (VIII).

4.8 Grams (1 mol.) of 2-nitrohomoveratric acid were first converted into the acid chloride in the following manner. The weighed amount of acid is covered with 20 c.c. of chloroform, cooled in water, and gradually treated with 4.2 grams (1.01 mol.) of phosphorus pentachloride in small quantities at a time; the chlorination proceeds somewhat rapidly, and is accompanied by a brisk evolution of hydrogen chloride along with a considerable rise in temperature. As soon as the main reaction is over, the resultant red solution is gently warmed on the water-bath for a short time, that is, until the evolution of hydrogen chloride ceases, and then the phosphoryl chloride is removed as completely as possible by evaporation in a vacuum at a temperature not exceeding  $55^{\circ}$ . The last traces of phosphoryl chloride, which cling very tenaciously to the residue, can conveniently be removed by dissolving the contents of the distilling flask in dry benzene and repeating the evaporation in a vacuum. In order to facilitate the subsequent coupling with  $\beta$ -phenylethylamine, the residual glassy mass is dissolved in a very small quantity of dry benzene, and this solution is then added in small portions, and alternately with 6 c.c. of 20 per cent. aqueous sodium hydroxide (1.5 mol.) to 2.4 grams (1 mol.) of  $\beta$ -phenylethylamine suspended in 10 c.c. of water, the whole being well cooled in a freezing mixture and continuously shaken. As soon as the whole of the chloride is consumed, the amide which is formed is dissolved in 50 c.c. of benzene, washed with a little water, and finally with dilute acid. The dried benzene solution is submitted to fractional precipitation with light petroleum. The first precipitate obtained contains principally resinous impurities, and is rejected. The clear liquid filtered from it, when treated hot with light petroleum until a precipitate begins to form, and then allowed to cool slowly, yields first an oil, but this soon crystallises in aggregates of pointed prisms, which are collected, the filtrate being subsequently treated in a similar manner.

A third crystallisation is difficult to obtain an account of the solubility of the amide in a large volume of light petroleum, and in this case it is advisable to evaporate the solution to dryness and crystallise the residual resin from a mixture of benzene and light petroleum. By recrystallising the product once more from the same solvent-mixture, it is obtained pure for analysis in almost colourless, thick prisms, which are finally dried over sulphuric acid in a vacuum desiccator:

0.1616 gave 0.3709  $\text{CO}_2$  and 0.0855  $\text{H}_2\text{O}$ .  $\text{C}=62.6$ ;  $\text{H}=5.92$ .

0.2260 „ 16.4 c.c.  $\text{N}_2$  at  $19^\circ$  and 720 mm.  $\text{N}=7.93$ .

$\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2$  requires  $\text{C}=62.75$ ;  $\text{H}=5.87$ ;  $\text{N}=8.14$  per cent.

The melting point of 2-nitrohomoveratroyl- $\beta$ -phenylethylamine lies at about  $86^\circ$ , with slight previous softening. By recrystallising from hot toluene, the melting point rises to  $98^\circ$ .

*Attempted Cyclisation of 2-Nitrohomoveratroyl- $\beta$ -phenylethylamine.*

With the object of bringing about the cyclisation of 2-nitrohomoveratroyl- $\beta$ -phenylethylamine to form nitroveratryldihydroisoquinoline, according to the scheme (VIII—IX) given on p. 950, we operated according to the method indicated above, and heated the first of these two substances with an excess of phosphoric oxide in solution in toluene. Here we found, however, contrary to all our preceding experience, that the elimination of water is slow and difficult. It is no longer sufficient to heat to boiling for three to five minutes only to produce the dehydro-compound; the heating must be continued for fifteen or thirty minutes, and even then the reaction is still incomplete. After shaking the product with water, we proved that the aqueous layer did not contain the least trace of a basic substance, and failed to give a precipitate with sodium carbonate. The whole of the product remains in solution in the toluene layer, which yields a yellow-coloured residue on evaporation to dryness. The major portion of the latter consists of the original substance, unchanged. By recrystallisation from toluene, we succeeded, nevertheless, in isolating a new substance from the yellow residue, which it contains to the extent of 20 to 30 per cent., and to which the yellow coloration is due. This yellow compound clearly constitutes the product of dehydration, for its analysis certainly leads to the formula  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_2$ , which contains one molecule of water less than the original 2-nitrohomoveratroyl- $\beta$ -phenylethylamine:

0.1132 gave 0.2749  $\text{CO}_2$  and 0.0516  $\text{H}_2\text{O}$ .  $\text{C}=66.23$ ;  $\text{H}=5.10$ .

0.0860 „ 7.0 c.c.  $\text{N}_2$  at  $20^\circ$  and 717 mm.  $\text{N}=8.81$ .

$\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_2$  requires  $\text{C}=66.22$ ;  $\text{H}=5.58$ ;  $\text{N}=8.58$  per cent.

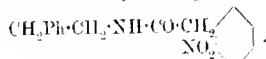
This compound separated from boiling toluene in yellow crystals, melting at  $129^\circ$ . It is absolutely devoid of basic properties, being

insoluble in hydrochloric acid, even when concentrated, and reacts neither with methyl iodide nor with methyl sulphate.

Supposing that, in spite of its properties, it might constitute the required nitroveratryldihydroisoquinoline, we submitted it to reduction in the hope of converting it into aminoveratryltetrahydroisoquinoline. It was therefore heated with stannous chloride and concentrated hydrochloric acid. On cooling, a well-defined, crystalline tin salt, sparingly soluble in cold water, was obtained, which, when decomposed with hydrogen sulphide, yielded a colourless, crystalline hydrochloride, freely soluble in water. This hydrochloride gives a precipitate with auric chloride and platinic chloride, but not with picric acid. The addition of an alkali causes the separation of an oily base ammoniacal in odour.

This base is a primary one (carbylamine reaction), and in order to identify it, we transformed it, according to the Schotten-Baumann reaction, into its benzoyl derivative. The latter crystallises from alcohol or water in spangles, melting at  $118^{\circ}$ . Its analysis (Found, C=80.06; H=6.60) leads to the formula of benzoyl  $\beta$ -phenylethylamine ( $C_{15}H_{15}ON$  requires C=79.96; H=6.22 per cent.), and evidently the two substances are identical, for a mixture of the two melts at  $118^{\circ}$ , the melting point of each of them separately. The base obtained by the reduction of the yellow compound, melting at  $129^{\circ}$ , is therefore  $\beta$ -phenylethylamine. It consequently follows that the so-called yellow substance is in no way a derivative of isoquinoline, and that the treatment of 2-nitrohomoveratroyl  $\beta$ -phenylethylamine with phosphoric oxide does certainly bring about the elimination of water, but without cyclisation. The dehydro-product is still a derivative of  $\beta$ -phenylethylamine, capable of regenerating that base by reduction, accompanied by hydrolysis. We have already indicated our views on its constitution.

We may add that we have attempted, with the same negative result, the cyclisation of the simpler compound:



This substance, obtained by the action of the chloride of  $\alpha$ -nitrophenylacetic acid on  $\beta$ -phenylethylamine, forms colourless crystals, melting at  $97-99^{\circ}$ :

0.1207 gave 0.2986  $CO_2$  and 0.0608  $H_2O$ . C=67.47; H=5.64.

$C_{16}H_{16}O_2N_2$  requires C=67.58; H=5.67 per cent.

When heated for half an hour with excess of phosphoric oxide in xylene solution, it undergoes no change whatever.

A third crystallisation is difficult to obtain an account of the solubility of the amide in a large volume of light petroleum, and in this case it is advisable to evaporate the solution to dryness and crystallise the residual resin from a mixture of benzene and light petroleum. By recrystallising the product once more from the same solvent-mixture, it is obtained pure for analysis in almost colourless, thick prisms, which are finally dried over sulphuric acid in a vacuum desiccator:

0.1616 gave 0.3709  $\text{CO}_2$  and 0.0855  $\text{H}_2\text{O}$ .  $\text{C}=62.6$ ;  $\text{H}=5.92$ .

0.2260 „ 16.4 c.c.  $\text{N}_2$  at  $19^\circ$  and 720 mm.  $\text{N}=7.93$ .

$\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2$  requires  $\text{C}=62.75$ ;  $\text{H}=5.87$ ;  $\text{N}=8.14$  per cent.

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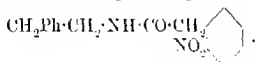
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# XCIX.—*A Criticism of Some Recent Viscosity Investigations.*

By EUGENE COOK BINGHAM.

As scientific knowledge increases in volume, it becomes increasingly difficult to become fully informed even in the narrow field within which one happens to be working. It therefore happens that truth once discovered is apparently lost, only to be rediscovered and lost again, instead of becoming at once the property of all, with the consequent saving of time and energy. Nowhere is this more noticeably true, perhaps, than in the study of viscosity. The reason may be that few workers have been interested in the property of viscosity for its own sake, but hundreds of researches have been carried out in the hope of throwing light upon problems suggested by other properties, such as conductivity, dissociation, etc.

Viscosity data are in a rather unsatisfactory condition. Only part of the data is given in absolute units, so that comparisons are difficult. Furthermore, much of the data, which is given in absolute units, was obtained from measurements which were not themselves absolute, but relative, and it appears that in relative measurements the necessary corrections have often been omitted whereby reduction to absolute units could be effected with sufficient precision. Thus, test observations by workers using the same liquid for successive observations have been known (Pfitzinger and Handl, *Sitzungsber. K. Akad. wiss. Wien*, 1878, **78**, ii, 113; compare Thorpe and Rodger, *Phil. Trans.*, 1891, **185**, A, 403) to differ by over 10 per cent. The earlier absolute measurements were also somewhat discordant, owing to the fact that several important corrections were overlooked. As a result of these conditions, several (Knibbs, *J. Roy. Soc. New South Wales*, 1896, **30**, 186; compare *Zeitsch. physikal. Chem.*, 1912, **80**, 685; Traube, *Ber.*, 1886, **19**, 871) have expressed the doubt as to the possibility of the accurate measurement of viscosity. However, it has now been proved that with the necessary corrections which can be easily applied, perfectly definite and very accurate values may be obtained. Perhaps the best proof of this is the fact (compare *Zeitsch. physikal. Chem.*, 1912, **80**, 685) that the mean deviation from the mean values for water from 0° to 100° of six different investigators is only 0.3 per cent.

In view of the scantiness of existing material, it is therefore a matter for particular regret when a research, planned with the view toward the highest possible accuracy, is carried out without

the knowledge of conditions and corrections necessary for making the results truly absolute, and therefore comparable with the data of other observers, and of the appropriate methods for interpreting the results.

The recent work of Applebey (T., 1910, **97**, 2000) may be chosen as an illustration because this work has been carried out with admirable care and ingenuity. The attempt was made to reduce the error to less than 0.1 of 1 per cent., and control experiments are given to prove that this high degree of precision was actually attained. Applebey states on p. 2013: "It is to be noted that no kinetic energy correction is to be applied in calculating the results of experiments with viscometers in which the capillary opens out into a reservoir of the same liquid. The correction calculated by earlier observers (Hagenbach, *Pogg. Ann.*, 1860, **109**, 385; Finkener, see Gartenmeister, *Zeitsch. physikal. Chem.*, 1891, **6**, 524) is only applicable when the liquid flows from the capillary directly into the air. In viscometers of the Ostwald type, however, the gain of kinetic energy at the beginning of the capillary is balanced by the loss of kinetic energy on emerging from the capillary into the lower bulb. The net increase in kinetic energy is therefore negligible. . . ." The present author holds that the correction which is necessary when the capillary opens into the air is not a kinetic energy correction at all, but rather a correction for the loss of pressure due to the capillary attraction at the opening of the tube. This correction is dependent upon the shape of the end of the tube, and it fluctuates with the size of the drop at a given moment, hence it is very difficult to estimate. Naturally this correction is avoided in viscometers of the Ostwald type. It would be presumptuous to attempt to prove that the kinetic energy correction does indeed apply to the Ostwald type of viscometer in view of the published work of Neumann ("Vorträge über Hydrodynamik"), Jacobson (*Arch. f. Anat. u. Physiol.*, 1860, **80**), Conette (*Ann. chim. Phys.*, 1890, [vi], **21**, 433), Wilberforce (*Phil. Mag.*, 1891, [v], **31**, 407), Knibbs (*J. Roy. Soc. New South Wales*, 1893, **29**, 77; 1896, **30**, 186), Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, A, 397), Boussinesq (*Compt. rend.*, 1890, **110**, 1160, 1238; 1891, **113**, 9, 49), and Brillouin ("La Viscosité," Gauthier-Villars, 1907, p. 131), in addition to those mentioned by Applebey. A simple statement may, however, serve to make the necessity for the correction apparent. For sake of simplicity, let us assume that the liquid flows through a horizontal capillary of uniform bore connecting two reservoirs. If  $P'$  is the hydrostatic pressure at the entrance of the capillary and  $P''$  at the exit, then  $P' - P''$  is the measure of the pressure used up in overcoming the

viscous resistance. Near the entrance to the capillary, however, the liquid is in accelerated motion for a short distance. In gaining this kinetic energy, the pressure falls from  $P$  to  $P'$ , hence the whole loss in pressure, measured by the difference in heads in the two reservoirs, is equal to  $P - P' + P' - P'' = P - P''$ . The mean velocity at the exit end of the tube is the same as at every other cross-section of the tube, and its inertia carries it a considerable distance into the body of the liquid in the lower reservoir. By means of eddies, this motion finally becomes disordered, that is, it disappears as heat, and not as potential energy, as Applebey supposes. Finally, Bingham and White (*Zeitsch. physikal. Chem.*, 1912, **80**, 681) measured the viscosity of water under the above conditions with a capillary which was afterwards cut into several pieces so as to give conditions for interrupted flow, and it was found that the kinetic energy corrections as demanded by the theory are directly proportional to the number of capillaries in series.

By varying the pressures, Applebey finds that the product of the pressure multiplied by the time of transpiration is approximately constant only when the time is not less than 400 seconds. He apparently assumes (p. 2005) that the inconstancy of the product  $p \times t$  for smaller values of  $t$  is "due to the fact that above a certain limiting velocity the flow of liquid in the viscometer is not steady, but that some of the potential energy is expended in forming eddies within the liquid." There can be no doubt that the product  $p \times t$  will become inconstant when the velocity of efflux becomes sufficiently great, but the cause in Applebey's experiments may be due to the kinetic energy correction, which he has considered negligible. His capillary had a radius of 0.2 mm., and the transpiration volume was 7 c.c. Therefore the velocity of efflux could never have been greater than:

$$\frac{V}{\pi r^2 t} = \frac{7}{3.1416 \times (0.02)^2 \times 400} = 14 \text{ cm. per second.}$$

Now, Osborne Reynolds (*Phil. Trans.*, 1883, **174**, 935; 1886, **177**, 4, 157) has given an expression for the critical velocity above

which eddy currents may be formed. It is  $\frac{7^{(10)}}{rp\phi}$ . For water at 25° the fluidity ( $\phi$ ) is equal to 112.0 and the density ( $\rho$ ) is not far from unity, hence the critical velocity is 312 cm. per sec. All of Applebey's solutions were more viscous than water at 25°, hence his velocities were not one-twentieth of the critical value where the motion becomes sinuous.

Moreover, not only was the fancied danger of sinuous motion unreal, but the very slow velocities which were used tended to aggravate a source of error which in this particular case became



very annoying (pp. 2010, 2011, and 2012). He says in particular that "in spite of all precautions, the tubes frequently became contaminated with dust." At very low velocities, particles of dust could more easily find lodgment in the capillary, and thus vitiate the determination. That higher velocities would have served to keep the capillary clean is indicated by the results of several experimenters,\* where with reasonable care to avoid the presence of dust the successive observations are almost invariably quite satisfactory.

The equation for viscosity containing the correction for the loss in kinetic energy is:

$$\eta = \frac{\pi g r^4 t p}{8 l t'} - \frac{m \rho l'}{8 \pi t'}$$

where  $\pi = 3.1416$ ,  $g$  is the acceleration due to gravitation,  $r$  the radius of the capillary,  $l$  its length,  $t$  the time of transpiration,  $l'$  the volume passing through the capillary,  $p$  the corrected pressure in grams per sq. cm.,  $\rho$  is the density of the liquid, and  $m$  is a constant which has been approximated to be 1.12 (compare *Zeitsch. physikal. Chem.*, 1912, **80**, 670). The correction for kinetic energy is expressed by the second term of the right-hand member of the equation. For a given instrument, the equation takes the form:

$$\eta = ct p - c' \rho / t,$$

where  $c$  and  $c'$  are constants. Since the density cannot be changed *ad libitum*, the only way to make the kinetic energy correction negligible is to make the time of transpiration very large. This is exactly what was done by Applebey, and I believe that his measurements possess a higher degree of trustworthiness than many of the measurements which have been made with this type of apparatus. Apart, however, from the danger of partial clogging of the capillary, such lengthening of the time of transpiration is objectionable, both on account of the increased difficulty in proper temperature regulation and in the loss of time occasioned. Some of Applebey's measurements required over two hours for a single transpiration, whilst the minimum was seven minutes. With several modern forms of apparatus, less than half of the minimum time used by Applebey is required, and by employing variable pressure the time consumed with the more viscous liquids need not necessarily be any greater. With the Ostwald type of apparatus, having a pressure which is not variable at will, the loss of time with the more viscous liquids makes the use of a series of viscometers, with the consequent loss of time in calibration and additional sources of error, almost a necessity.

Particularly worth study in this connexion are the very consistent results of Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, A, 397).

If two liquids having viscosities  $\eta_1$  and  $\eta_2$  transpire through a given instrument in times  $t_1$  and  $t_2$  respectively, we have the relation:

$$\eta_1 = \frac{c_1 p_1}{t_1} - \frac{c_2 p_2}{t_2}$$

and if  $t_1$  and  $t_2$  are both very large, and also if, in addition,  $\eta_1$  is nearly equal to  $\eta_2$ , this expression can be reduced to the form:

$$\eta_1 = \eta_2 \frac{t_1 p_1}{t_2 p_2}$$

which is the formula given by Ostwald and Luther ("Physiko-chemische Messungen," 2nd ed., Engelmann, p. 259 *et seq.*), and generally used for calculating viscosities with the Ostwald viscometer. Of course, these two expressions are not generally identical, and it is the oversight of this fact which seems to have often led observers into error. It is obvious that in using the Ostwald instrument a ready means of control can be obtained by measuring the viscosities of several different liquids, or of the same liquid at considerably different temperatures to see how closely the results would agree with those by the absolute method. The results of such tests have only rarely been given, and then they do not inspire confidence (*Amer. Chem. J.*, 1911, **46**, 281; compare Findlay, *Zeitsch. physikal. Chem.*, 1909, **69**, 203).

In the Ostwald type of apparatus it seems to be regarded as of great importance that the height of the hydrostatic column should be small, thus keeping the velocity of flow small while using a capillary of fairly large diameter. In Applebey's apparatus this height was 10.8 cm., so that an error of 0.01 cm. in adjusting the height would cause an appreciable error. It is probably to avoid this source of error that the bulbs above and below the capillary are made large. There is, however, comparatively bad drainage on the surfaces which depart widely from the vertical, the adjustment of temperature is slow in large, spherical masses, and the time of transpiration is made unnecessarily large. Finally, with this method the specific gravity of each liquid at every temperature which it is proposed to study must also be known to 0.1 of 1 per cent.\*

In the interpretation of viscosity data, it may be pointed out that many years ago it was shown (T., 1897, **71**, 374) that viscosity curves of mixtures are rarely linear, but that the values are usually less than they should be on the usual assumption that viscosities are normally additive. It was, however, pointed out (Jones and Bingham, *Amer. Chem. J.*, 1905, **34**, 515; Bingham, *ibid.*, 1906,

\* In some other forms of apparatus it is only necessary to know the specific gravity approximately, since it is only used in calculating correction terms.

35, 195; *J. Amer. Chem. Soc.*, 1911, **33**, 1257; *Physical Review*, 1912, **35**, 407) that theoretically we should expect fluidities to be additive, so that viscosities cannot be additive as has been assumed, but must normally be hyperbolic. Existing viscosity data fully confirm this view. Numerous papers have been published (for a partial bibliography compare *Physical Review*, 1912, **35**, 407; also White, *J. Ind. Eng. Chem.*, 1912, **4**, 267) showing that fluidities are satisfactorily additive, provided that association and dissociation do not enter as disturbing factors. It is perhaps unfortunate that this proviso must be attached, since it seems to offer an opportunity for "making the facts fit the theory." The assumption of association should, however, never be resorted to without supporting evidence. Thus it would be difficult to explain how the fluidity of a mixture could be greater than the value obtained from the linear fluidity curve unless one or more of the components of the mixture are themselves associated. If, however, on mixing two components heat is evolved, contraction occurs, and the fluidity is less than that calculated from the linear fluidity curve, a suspicion may justly be aroused that the abnormality is due to combination. When it can be shown that the maximum heat evolution, contraction, lowering of the vapour pressure, and lowering of the fluidity all coincide in the same mixture, and that, moreover, this mixture contains simple molecular proportions of the constituents, and particularly when it can be shown that the combination between the components obeys the law of mass action, as in the case of chloroform and ether (*Zeitsch. physikal. Chem.*, 1913, *in press*; compare *Physical Review*, 1913, **36**, 112 *et seq.*), then there is not only justification for the assumption of combination, but the cases excepted in the above proviso become positive aids in substantiating the hypothesis that fluidities and not viscosities are additive.

The authors of several recent papers have accepted the earlier assumption that viscosities are additive, without a reference to the work just cited. Thus, Baker (T., 1912, **101**, 1409), in a valuable paper on the viscosities of mixtures of alcohols and ethers, notes with surprise that the values of the viscosity are less than would be expected on the old hypothesis. In view of the later hypothesis, this fact is not only not surprising, but has been predicted beforehand for most mixtures. He says, "In nearly all cases there is a considerable departure from the calculated values, and in two cases a minimum value for the viscosity was observed. These results indicate that when the associated alcohols are mixed with ethers, dissociation of the former takes place, and therefore the viscosity of the mixture is less than that calculated from the

viscosity of the components." I do not question the correctness of Baker's conclusion that dissociation does occur in at least some of the cases discussed by him; but the reading of his discussion is not so convincing as it might be, since he does not attempt to establish his fundamental assumption that viscosities are normally additive in homogeneous mixtures.

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*C. Reactions of Halogen-substituted Acids. Effect of Alkalis in Methyl-alcoholic Solution on Bromoacetic,  $\alpha$ -Bromopropionic, and Monobromosuccinic Acids.*<sup>3</sup>

By ERIK HÖST MADSEN.

In reactions between organic halogen compounds and alcoholic alkalis, it is customary to use sodium ethoxide in order to bring about substitution, and alcoholic potassium hydroxide for the elimination of hydrogen haloid. Hitherto, however, no theoretical or practical reasons have been given for using the different reagents in the respective cases.

Nef (*Annalen*, 1899, **309**, 126) was the first to investigate the reactions of a large number of alkyl haloids, and in all cases he obtained the same results, whether sodium alkylsides or alcoholic solutions of potassium hydroxide were used. In many cases elimination of hydrogen haloid and substitution took place simultaneously, and he concluded that the action of the two reagents was essentially the same, the course of the reaction depending only on the position of the halogen atom and on the character of the alkyl group.

The halogen-substituted acids behave similarly. In those of them which contain two or more halogen atoms, it is possible for the same reagent to bring about both kinds of reaction simultaneously at the different halogen atoms. Thus, on treating dibromopropionic acid with two molecules of sodium ethoxide, or of potassium hydroxide in alcoholic solution, hydrogen bromide is eliminated, with the formation of monobromocrylic acid (Merz, "Studien über gebromte Propionsäuren," Erlangen, 1889, p. 15). When three

<sup>3</sup> For fuller details, reference should be made to the author's book, "Kritiske Studier over Alkoholater og Baser Indvikling i et organiske Halogenforbindelser," Copenhagen, 1912, Pp. 92-157.

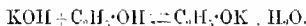
molecules of potassium hydroxide are used in alcoholic solution, replacement of the second bromine atom also occurs, with the formation of ethoxyacrylic acid.

The results of some investigations seem to indicate, however, that sodium ethoxide and alcoholic potassium hydroxide may act differently. Thus, Hell and Lauber (*Ber.*, 1874, **7**, 560) found that ethyl  $\alpha$ -bromobutyrate and hot alcoholic potassium hydroxide gave mainly crotonic acid, with very little ethoxybutyric acid. Duvillier (*Ann. Chim. Phys.*, 1879, [v], **17**, 532) found that the same ester gave only ethyl ethoxybutyrate when sodium ethoxide was used.

It is probable that the above differences are due to variations in temperature and concentration of the reagents in the different experiments, and not to any essential difference in the actions of sodium ethoxide and alcoholic potassium hydroxide. For example, Schreiner (*Annalen*, 1879, **197**, 1), in the reaction between ethyl bromobutyrate and sodium ethoxide, in one experiment obtained ethyl crotonate, and in another, ethyl ethoxybutyrate.

The above few examples would indicate that no distinction can be drawn between alcoholic solutions of hydroxides and alkoxides of the alkali metals, with respect to the elimination of hydrogen haloid or to the process of substitution. Both reactions are due to the alkoxide, which is the only compound, except alcohol, that is common to both solutions when absolute alcohol is used.

In alcoholic potassium or sodium hydroxide solution, an equilibrium exists in accordance with the equation:



The position of equilibrium is not known, but the results of investigations hitherto carried out would indicate that in such solutions most of the alkali metal is present as the alkoxide, and that a large quantity of water is necessary to decompose this compound. The presence of water in such solutions has the effect that they are able to react in such a way that the halogen is substituted by the hydroxyl group, as well as by the ethoxy-group. The alkyl haloids are not suitable for observing the simultaneous occurrence of these two reactions, since even with 50 per cent. aqueous alcoholic solutions the formation of ether is the main reaction.

The halogen-substituted acids, in most cases, give either alkoxides or else unsaturated acids, or generally a mixture of both, when treated with alcoholic potassium hydroxide. In some cases, however, the hydroxide character of the solution is very marked, hydroxy-acid being formed in addition to the alkoxo-acid; as examples may be quoted bromoisosuccinic acid (Tanatar, *Annalen*, 1893, **273**, 40) and bromoisobutyric acid (Bischhoff, *Ber.*, 1891, **24**, 1041).

Walden, in his well-known investigations on optical inversion (*Ber.*, 1896, **29**, 133; 1897, **30**, 2795, 3146; 1899, **32**, 1833), obtained only malic acid from the optically active halogen-substituted succinic acids, no matter whether the alkali used was in aqueous or in methyl-alcoholic solution. Walden was not concerned as to the reason why the formation of the methoxy-acid was totally restrained, confining himself to the optical results; the author has consequently submitted the matter to further investigation in order to find out how much water (in the form of water or hydroxide) the alkaline solution must contain in order to do away completely with the formation of methoxy-acid. Inactive bromosuccinic acid was used, since optical properties were of no importance in this connexion.

Preliminary experiments having shown that the reaction took place much more rapidly in methyl-alcoholic sodium hydroxide solution than in a solution of sodium ethoxide in absolute methyl alcohol, it seemed probable that there would be some connexion between the reaction-velocity and the products formed when the alcoholic solution used contained varying quantities of water. In order to test this supposition more thoroughly, the investigation was extended to include  $\alpha$ -bromopropionic and bromoacetic acids, as well as monobromosuccinic acid.

It is necessary to know exactly the composition of the solution used. In the case of sodium methoxide solution, there is no difficulty in this connexion if absolute methyl alcohol is used, but if the methyl-alcoholic solution of sodium hydroxide is prepared by dissolving the hydroxide in the alcohol, the water content of the solution is not known. The method adopted in the latter case was to add a definite quantity of water to the methoxide solution, or else to dissolve sodium in a mixture of known composition of methyl alcohol and water.

#### EXPERIMENTAL.

##### *Purification of Substances Used.*

Anhydrous methyl alcohol was obtained by three repeated distillation from metallic calcium (compare Klason and Norlin, *Arkiv Kem. Min. Geol.*, 1905, **2**, 24).

Bromoacetic acid was purified by recrystallising Kahlbaum's product from one-fifth of its weight of benzene, it being afterwards dried over phosphoric oxide and paraffin. The equivalent was 139.6 (theory 139.0).

$\alpha$ -Bromopropionic acid was purified by drying Kahlbaum's product in a current of air at 125°, distilling it under diminished pressure, and causing it to crystallise by cooling with solid carbon

dioxide and ether. The crystals were centrifugalised for fifteen minutes at the ordinary temperature, kept overnight in a vacuum desiccator, and again centrifugalised the next day, after which they were dried for nearly a week in a vacuum desiccator. The melting point was  $25.7-27.1^{\circ}$ , the equivalent being  $153.6^{\circ}$  (theory  $155.0^{\circ}$ ).

Commercial monobromosuccinic acid contains fumaric acid. It was purified in two ways: (1) According to Müller's method (*Zeitsch. physikal. Chem.*, 1902, **41**, 486), by solution in water and extraction of the fumaric acid with ether, the process being repeated four times. (2) By fractional recrystallisation of the acid, which had been treated twice according to Müller's method. Thirty-nine grams of the acid were dissolved (incompletely) in 100 c.c. of acetone, and to the filtrate 90 c.c. of benzene were added. The solution was then concentrated until it crystallised on cooling; the first fraction which separated contained all the fumaric acid, the succeeding fractions consisting of practically pure monobromosuccinic acid. The product (1), afterwards referred to as the extracted acid, had an equivalent of 98.3, the product (2), called the recrystallised acid, an equivalent of 98.6--98.8 (theory 98.5).

#### *Examination of Reaction Products.*

The reaction product to be expected may consist of methoxy- or hydroxy-acids, or a mixture of both. Since it is impossible to isolate the respective acids without considerable loss of substances, the method adopted was to estimate the percentage of the methoxy-group in the product obtained. The actual formation of hydroxy-acid in any particular case could only be proved by isolating it, owing to the absence of distinctive tests for identification.

In all cases the solutions used were prepared with absolute methyl alcohol, and were 0.1 molecular with respect to the sodium salt of the acid; they also contained sodium methoxide and water in such proportions that the reaction mixture was represented by 1 mol. of the sodium salt of the acid, 1 mol. of sodium methoxide, and 0, 1, or 3 mols. of water. The respective solutions will be called *A*, *B*, or *C*, according as the proportion of water is 0, 1, or 3 mols. The reaction took place in sealed tubes, which were heated in a thermostat at  $61^{\circ}$ ; when the reaction was finished, the contents of each tube were poured into a dish and evaporated to dryness on the water-bath. The last traces of methyl alcohol were removed by dissolving the residue in 10 c.c. of water, neutralising with hydrochloric acid, and again evaporating to dryness. The residue was powdered, well mixed, and the percentage of methoxyl determined in a weighed portion. The accuracy of the method was checked by a blank experiment with succinic acid.

The results obtained with bromosuccinic acid are shown in the following table:

	A.	B.	C.
Mols. of substance used .....	0.01	0.01	0.01
Time .....	21 days	95 hours	67 hours
Weight of residue (grams) .....	2.86	2.71*	3.02
Grams of methoxyl in residue .....	0.00408	0.00068	0.00029
Per cent. of methoxy-acid formed ...	49.8 †	6.8	2.9

Experiment C confirmed the results obtained by Walden, but for complete verification it was necessary to isolate the malic acid. This was done as follows: 3.94 grams (0.02 mol.) of recrystallised bromosuccinic acid were dissolved in 100 c.c. of absolute methyl alcohol; after the addition of a solution of 1.38 grams (0.06 mol.) of sodium in a mixture of 1.08 grams (0.06 mol.) of water and 100 c.c. of methyl alcohol, the mixture was heated for seven hours on the water-bath under reflux, a calcium chloride tube being attached to the condenser. On the next day the precipitated sodium salts were collected (by centrifugalising), washed with absolute methyl alcohol, and dried in a vacuum, after which the salts were dissolved in 2 grams of water, and the fumaric acid precipitated with a little dilute sulphuric acid. After collecting the fumaric acid, the filtrate was diluted to 40 c.c., and the last traces of fumaric acid extracted with ether (total weight of fumaric acid = 0.34 gram). The solution was then freed from sulphuric acid by the addition of the exact equivalent of barium hydroxide, the malic acid precipitated as the lead salt, the precipitate washed with 60 per cent. alcohol, and then treated with hydrogen sulphide. The weight of racemic malic acid left on evaporation of the filtrate from the lead sulphide, any inorganic salts present having been removed by redissolving the acid in ether, was 0.59 gram. (Found, C = 36.15; H = 4.76. Calc., C = 35.81; H = 4.52 per cent.) The filtrate from the sodium salts still contained some fumaric (0.03 gram) and malic acids. By evaporation, extraction of the residue with acetone, renewed evaporation and fractional extraction of the residue with ether, 0.29 gram of yellow, but nearly pure, malic acid was obtained. Thus the total amount of fumaric acid formed was 0.37 gram (16 per cent. of the theory) and 0.88 gram of malic acid (33 per cent. of the theory).

These experiments confirm Walden's results, and disclose the

\* A little of the residue was lost, so that this number is too low.

† In the case of A, 64 per cent. of the bromosuccinic acid had reacted in 9 days, and 71 per cent. in 21 days, some fumaric acid being formed as well as methoxy succinic acid. Before the evaporation, 5 c.c. of water were added to prevent further formation of methoxy-acid, and if the percentage of methoxy-acid formed is corrected to 100 per cent. reaction of the bromosuccinic acid, the number 57.5 is obtained instead of 49.8.



noteworthy fact that one equivalent of water in the presence of a very large excess of methyl alcohol enters almost quantitatively into reaction.

The results obtained with  $\alpha$ -bromopropionic and bromoacetic acids are given in the following table:

	$\alpha$ -Bromopropionic acid.		Bromoacetic acid.	
	A.	C.	A.	C.
Mols. of substance used .....	0.005	0.005	0.005	0.005
Time (hours).....	97	97	25	25
Weight of residue (grams) .....	1.13	1.12	1.13	1.14
Grams of methoxyl in residue ...	0.00465	0.00438	0.00461	0.00451
Per cent. of methoxy acid formed	93.0	87.6	92.1	96.8

Thus in all cases about 90 per cent. of the theoretical quantity of methoxy-acid was formed, the presence of water having practically no effect on the course of the reaction.

#### Measurements of Velocity of Reaction.

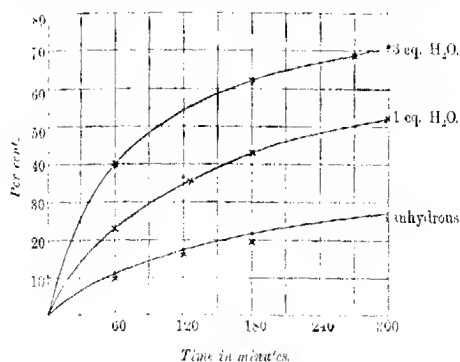
The reaction mixtures used corresponded with those given in the first part of this paper. They were made as follows, the acid and alkaline solutions being prepared separately. The acid solutions were 0.2-molar in all cases, the sodium methoxide solutions being as follows: (a) 0.4*N* for the experiments with monobasic acids, I anhydrous, II with 0.2 mol. water per litre, III with 0.6 mol. water per litre; (b) 0.6*N* for the experiments with the dibasic acid, I, II, and III being as in (a). When equal volumes of the acid and alkaline solutions were mixed, solutions were thus obtained corresponding with A, B, and C (p. 968). A fourth solution, D, was also used, which corresponded with A, but contained, in addition, 0.5 mol. of sodium bromide per litre. The solutions were mixed at the ordinary temperature, and then placed in sealed tubes in a thermostat at 64°, each tube containing about 20 c.c. of solution. The times, *t*, were calculated from a point ten minutes after the tubes were placed in the thermostat, and the concentration, *a*, of the reacting substances from the original titre of the acid solution;  $k_1$  and  $k_2$  are the constants calculated according to reactions of the first and second orders respectively. In calculating  $k_2$ , the factor 0.93948 was used to correct for alteration in volume on heating, no correction being applied in calculating  $k_1$ .

The following are the results for monobromosuccinic acid, the figures given relating to those obtained with the extracted acid (see p. 968).

A:—						B:—					
<i>t</i> .....	0	60	120	180	300	0	60	127	180	300	
200 ( $a-x$ )	18.13	16.43	15.21	14.55	13.45	17.62	13.55	11.42	10.09	8.41	
$k_1 \times 10^3$ ...	—	29.2	18.8	16.0	13.6	—	60.5	51.6	50.1	41.1	

$t$ , min.	0	60	180	270	$D$ :-	0	60	200	270
$k_1 \times 10^3$	16.92	10.18	6.43	5.26	16.11	13.21	10.83	9.91	
$k_2 \times 10^3$	—	139	114	103	—	47.7	32.2	30.6	

The results show that the reaction is accelerated by the addition of water (see diagram). The relation between the reaction velocities for  $A$ ,  $B$ , and  $C$  is approximately 1:4:8, but cannot be given exactly, since the values of  $k_2$  decrease continuously. That the decrease is not due to impurities in the acid is shown by the fact that both the extracted ( $\times$  in diagram) and recrystallised acids ( $\circ$  in diagram) give the same results. Nor is the decrease due to



sodium bromide formed during the reaction, as shown by experiment  $D$ , although the addition of sodium bromide has a noticeable effect on the velocity.

The results obtained with  $\alpha$ -bromopropionic acid are as follows:

$A$ :-	0	60	150	$D$ :-	0	60	120	180	240
$k_1 \times 10^3$	19.60	15.77	11.62	19.51	15.57	12.86	10.15	8.86	
$k_2 \times 10^3$	—	362	348	—	375	317	345	329	

$C$ :-	0	60	120	180	$D$ :-	0	60	120	180	240
$k_1 \times 10^3$	19.50	15.44	12.63	10.28	8.48	19.36	16.12	13.65	11.55	10.11
$k_2 \times 10^3$	—	370	332	356	345	—	365	291	287	271

The figures show that the presence of water has no effect on the velocity of reaction, the mean values of  $k_1 \times 10^3$  being 355, 349, and 358 in  $A$ ,  $B$ , and  $C$  respectively. The constants decrease slightly during the course of the reaction. When the strength of the (anhydrous) reaction mixture used is one-half that of  $A$ , they have a mean value of 280, which is somewhat lower than that for

the more concentrated solution. However, if the times necessary for the reaction to proceed to an extent of 50 per cent. are calculated in the two cases (.1 and 0.5*M*), they are found to be 233 and 199 minutes, giving a ratio of 1.17, which is sufficiently close to 1 to warrant the reaction being considered as one of the first order.

With bromoacetic acid, the results are as follows:

<i>A</i> —						<i>B</i> —					
<i>t</i> .....	0	60	110	161	230	0	60	105	150	210	
200 ( <i>a</i> — <i>x</i> )	18.03	10.51	7.82	6.37	4.86	17.91	10.63	8.07	6.46	4.78	
$k_2 \times 10^3$ ...	—	141	140	134	139	—	136	138	119	155	

<i>C</i> —						<i>D</i> —					
<i>t</i> .....	0	60	106	150	211	0	30	45	75	120	
200 ( <i>a</i> — <i>x</i> )	17.96	10.48	8.08	6.55	4.76	15.35	8.75	7.13	5.38	4.64	
$k_2 \times 10^3$ ...	—	141	137	138	136	—	349	355	313	334	

The mean values of  $k_2 \times 10^3$  for *A*, *B*, and *C* are respectively 139, 138, and 138, so that in this case also the presence of water has no effect on the velocity of reaction.

#### Discussion of Results.

In the case of the three acids examined there is evidently a connexion between the effect of water on the products formed and on the velocity of reaction. Whether the sodium salts of bromoacetic and  $\alpha$ -bromopropionic acids are treated with an anhydrous methyl-alcoholic solution of sodium methoxide, or with one containing 1—3 equivalents of water, a practically quantitative yield of the methoxy-acid is obtained; in accordance with this, the presence of water has no effect on the velocity of reaction. In the case of monobromosuccinic acid, however, the presence of water alters both the velocity of reaction and the products of reaction.\*

It is noteworthy that when the reaction is of the first order, the presence of sodium bromide, one of the products of reaction, decreases slightly the velocity of reaction, whereas when of the second or higher order, a considerable increase in velocity takes place.

The effect of water on the velocity of these reactions may be compared with its effect on the reaction between alkyl haloids and sodium alkylloxides (Lobry de Bruyn and Steger, *Rec. trav. chim.*, 1899, **18**, 311; *Zeitsch. physikal. Chem.*, 1904, **49**, 336), where the velocity is decreased by the addition of water; with small quantities of water the change is only relatively small, the velocity-constant in the case of ethyl iodide decreasing from 0.189 to 0.155 on the addition of 10 per cent. of water. In the case of the saponification

\* It is well to point out that these experiments show that conclusions based on a comparison of reaction velocities in mixed solvents must be drawn very cautiously.

of esters (Kremann, *Monatsh.*, 1905, **26**, 279), the addition of water has a much greater influence. In 0.05-molar solution the presence of 0.9 gram of water per litre increased the reaction velocity to four times its original value.

Whilst the results of the present investigation throw light on the problem it was the object of the author to examine, it is evident that the mechanism of the reactions taking place is in need of explanation. The constitution of the three acids would lead one to suppose that they would behave similarly; nevertheless the order of reaction is different in every case. That the reaction with bromoacetic acid is of the second order is in accordance with the chemical equation. The reaction with  $\alpha$ -bromopropionic acid is of the first order, however, and one may assume that the reaction does not take place between the salt (sodium  $\alpha$ -bromopropionate) and sodium methoxide, but between the salt and alcohol, the concentration of the latter remaining constant. The reaction between sodium bromosuccinate and sodium ethoxide is apparently of a higher order than the second. It is possible, according to the usual interpretation, that in this case two reactions are proceeding simultaneously with different and measurable velocities, namely: (1) the formation of an intermediate compound, and (2) its decomposition (compare Senter, *Ber.*, 1912, **45**, 2318; Senter and Ward, *T.*, 1912, **101**, 2534; Hohnberg, *Ber.*, 1912, **45**, 1713). It is possible, and even probable, that the decomposition of the intermediate compound by alcohol takes place with much more difficulty than the decomposition by water, so that mainly hydroxy-acid is formed, even in the presence of only small quantities of water, which is in accordance with the experimental results. In this connexion attention should be called to the fact that monobromosuccinic acid gives less than the calculated yield of methoxysuccinic acid when treated with anhydrous sodium methoxide solution. This fact is not easy to explain unless the formation of an intermediate product is assumed which is relatively stable in the presence of methyl alcohol, and therefore able to exist to some extent in a reaction mixture which contains only that alcohol as solvent, but is decomposed at once when water is added.

The author desires to express his thanks to Prof. E. Büllmann, in whose laboratories the experimental part of this investigation was carried out.

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*Cl.—Cyanogen Bromide and Cyanogen.*

By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

CYANOGEN bromide, in cold aqueous solution, or in the presence of such dilute acids as do not of themselves chemically decompose it, shows no evidence of suffering ionic dissociation. The dilute aqueous solution has the same odour as the solid compound; even after long keeping it yields with silver nitrate no turbidity; it is neutral to litmus, and the pungent vapour fails to give the guaiacum and copper sulphate reaction for hydrogen cyanide; moreover, the solution is a very feeble conductor of electricity.

Although the mixture produced by treating cyanogen bromide with alkali hydroxide contains but alkali bromide and alkali cyanate, Chattaway and Wadmore are of opinion (T., 1902, 81. 193) that hypobromite must first be formed, and then reduced.

That cyanate is not directly formed in the reaction with alkali hydroxide is proved from the following facts:

(1) Alkali cyanate is not reduced to cyanide by hydriodic acid, ferrous sulphate and alkali, sulphurous acid, alkali sulphite, or even by treatment with aluminium and alkali hydroxide. Further, it has no action on carbamide, either alone or in presence of alkali.

(2) If cyanogen bromide is treated with alkali iodide, followed by alkali, the mixture contains cyanide, but no cyanate, and, when acidified, yields free iodine.

(3) If it is treated with ferrous sulphate, and subsequently with alkali and ferric salt, the mixture on acidification gives Prussian-blue, but contains no cyanate.

(4) The bromide, if mixed first with sodium sulphite and then with alkali, contains sulphate and cyanide; no cyanate is present.

(5) A moderately concentrated solution of cyanogen bromide, mixed with carbamide, effervesces on the addition of alkali hydroxide, nitrogen being evolved; hypobromite therefore appears to be present. The mixture in this case contains not only cyanide but also some cyanate.

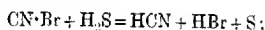
In cases (2) to (5) mentioned above, if the addition of the alkali hydroxide precedes that of the various reducing agents named, no reduction occurs. A direct experiment showed that hypobromite instantly converts potassium cyanide into the cyanate.

With very dilute solutions of carbamide no effervescence occurs, cyanate, but no cyanide, being formed; even with highly concentrated solutions, however, some cyanate is detectable. These phenomena are explained by the fact that carbamide tends to give derivatives in which the haloid element is joined to nitrogen (Chattaway,

*Proc. Roy. Soc.*, 1908, A, **81**, 381; T., 1901, **79**, 274); and since these behave as oxidising agents, the carbamide in such dilute solutions plays merely the part of a bromine-carrier; thus, when potassium cyanide (1 gram-molecule per litre) is oxidised by alkaline hypobromite (0.2 gram-molecule per litre), the volume-relations are unaffected by the previous addition of 1 molecule of carbamide for each molecule of cyanide present; but with hypobromite at five times the above concentration nitrogen escapes, and the proportion of hypobromite required to complete the oxidation is considerably greater than in the absence of the carbamide.

In all the above reactions the positive ion, joining the cyanogen, is eliminated as cyanide, the bromine being absorbed by the remainder of the molecule. The fact that water is non-ionised suffices to explain why it has no action on cyanogen bromide.

According to Chattaway and Wadmore (*loc. cit.*) hydrogen sulphide reacts quantitatively with cyanogen bromide, as shown by the equation:



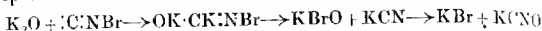
"a little" thiocyanic acid, however, being produced, the formation of which is attributed to the action of the sulphur on the hydrogen cyanide.

Our experimental results were as follows: A 2 per cent. solution of hydrogen cyanide, when shaken or gently warmed with flowers of sulphur, yielded with ferric chloride no red coloration; in presence of hydrogen bromide the same negative result was obtained. Various methods were tried of precipitating sulphur in solutions containing hydrogen cyanide or potassium cyanide acidified with hydrochloric acid; in no case (provided that the cyanide solution was kept acid) could any trace of thiocyanic acid be detected. Moreover, cyanogen bromide, when treated with potassium xanthate, yielded cyanide and a precipitate of sulphur, but no thiocyanic acid was found in the resultant mixture.

In order to determine the relative amount of thiocyanic acid produced in the reaction between cyanogen bromide and hydrogen sulphide, a dilute aqueous solution of the former was exactly saturated with a dilute solution of the latter; after removal of the sulphur by filtration, the thiocyanic acid contained in the clear liquor was determined by Barnes and Liddle's method; it was thus found that almost exactly one-half (0.505) of the cyanogen engaged had gone to form thiocyanic acid.

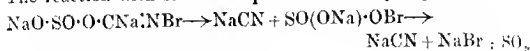
Since cyanogen bromide is not ionised by water or by dilute acids, it is natural to suppose that its chemical changes are brought about through union with the ionised fractions of the material presented, this union being followed by decomposition of the

resultant additive compound. In many cases that material cannot develop the higher valence of the nitrogen atom, whilst the carbon atom has available two valencies, through which this combination can take place; for example, the reaction with alkali hydroxide is represented thus:

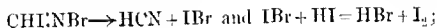


(no regard is here paid to the molecular structures of the products).

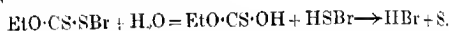
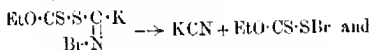
The reaction with sodium sulphite is similarly explained:



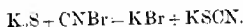
In the case of hydriodic acid:



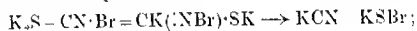
with potassium xanthate:



More difficult to explain is the reaction between cyanogen bromide and hydrogen sulphide, for  $HS \cdot CHI:NBr$  would yield  $HICN + HSB r$  instead of  $HSCN + HBr$ ; moreover, Gutmann has shown (*Ber.*, 1909, **42**, 3628) that when alkali sulphide is used the reaction proceeds in accordance with the equation:



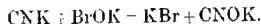
From analogy to the alkali oxide reaction the primary change in the case of alkali sulphide is:



then:



just as



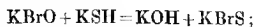
That potassium thiohypobromite is really produced and then desulphurised, as shown in these equations, receives support from the following facts.

(a) Alkaline solution of potassium sulphide, when mixed with potassium cyanide followed by acid, gives no reaction for thiocyanic acid.

(b) Potassium cyanide, mixed first with excess of alkaline hypobromite, next with alkaline sulphide, and then acidified, yields a liquid containing no thiocyanic acid (in other words, cyanate is not changed by alkali sulphide into thiocyanate).

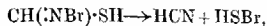
(c) The mixture of cyanide and sulphide, if treated with alkaline hypobromite and then acidified, reacts copiously for thiocyanic acid.

These facts may be interpreted as follows: alkali sulphide acting on the hypobromite thus:



the resultant thiohypobromite now transforms the cyanide into thiocyanate.

In the case of hydrogen sulphide it is possible that free thiohypobromous acid is first liberated, a portion of which decomposes forthwith, for sulphur is quickly (although not instantaneously) precipitated. Here the mechanism of the change is represented as follows:



the resultant thiohypobromous acid being desulphurised by the hydrogen cyanide. Since the former, however, if produced at all, very soon decomposes, the hydrogen cyanide, unless able to seize at once the whole of the available sulphur, must undergo more or less incomplete transformation into thiocyanic acid.

Consistent with this view is the fact that the presence of hydrochloric acid serves to inhibit the production of thiocyanic acid. If thiohypobromous acid is analogous to hypobromous acid, its decomposition must be accelerated by concentrated hydrochloric acid, with consequent diminution in the amount of available sulphur.

Conversely, whatever delays the decomposition of the thiohypobromous acid or accelerates the rate at which the cyanide can desulphurise it, favours the production of thiocyanic acid; alkali may act in either or both of these ways.

When aqueous hydrogen sulphide is used, the large bulk required tends to produce ultimately solutions of almost equal concentration; at the commencement of mixing, however, this is not the case; we have found that the variation in the amount of thiocyanic acid formed at different concentrations of the cyanogen bromide is quite readily appreciable.

Since the products of the change are hydrobromic acid, thiocyanic acid, hydrogen cyanide, and sulphur, alkalimetric determination of the total number of equivalents of acid formed from a known quantity of cyanogen bromide measures the amount of thiocyanic acid present in the mixture. This was checked by independent measurements of the total acidity from 2 molecules of bromide (with  $N/10$ -alkali and methyl-orange), and of the thiocyanic acid (by Barnes and Liddle's method), the result, by calculation from the total acidity, and by direct determination, showing a difference of 0.05 equivalent in the amount of thiocyanic acid.

In the experiment previously mentioned (p. 975), the cyanogen bromide being very dilute, for 2 molecules taken, 1.01 equivalents of thiocyanic acid were found present; in the latter ones, for the

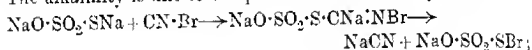


same amount of bromide (used at concentrations from one-tenth to five-tenths of a gram-molecule per litre), the corresponding figures for the thiocyanic acid varied from 0.85 to 0.59 equivalent. To observe further the effect of concentration, excess of gaseous hydrogen sulphide was brought into contact with a solution of cyanogen bromide, containing 1.2 decigram-molecules per litre; reckoned as before, the amount of thiocyanic acid was now 0.43 equivalent. From the results obtained it appears that the proportion of thiocyanic acid is highly variable.

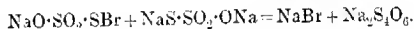
*Sodium Thiosulphate and Cyanogen Bromide.*

When cold neutral aqueous solutions were mixed, alkalinity was developed, lasting for one or two minutes; the final products were hydrogen cyanide, alkali sulphate, bromide, tetrathionate, thiocyanate, and sulphite.

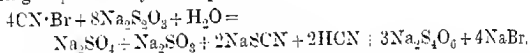
The alkalinity is due to the production of alkali cyanide:



then:



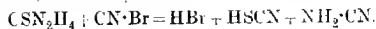
Next, the alkali cyanide reacts with the tetrathionate (see Marshall, T., 1908, **93**, 1729), producing hydrogen cyanide, together with alkali sulphate, sulphite, and thiocyanate, the complete interaction being expressed by the equation:



This was verified by the observations (i) that about one-half of the cyanogen in a known amount of the bromide went to form thiocyanate, and (ii) that when cyanogen bromide was treated with *N*/10-sodium thiosulphate, followed by *N*/10-iodine, the apparent molecular ratio of cyanogen bromide to thiosulphate consumed was 2:3; thus, four molecules of bromide absorb eight molecules of thiosulphate; but as the resultant mixture contains 1 molecule of sulphite, equivalent, so far as iodine-absorption is concerned, to two of thiosulphate, the apparent ratio of 4:6 is explained.

*Thiocarbamide in Aqueous Solution, and Cyanogen Bromide.*

If these are mixed in presence of sodium hydrogen carbonate (which has no action on the bromide) carbon dioxide escapes; the resultant solution contains sodium thiocyanate, sodium bromide, and cyanamide, but no cyanide:



If, instead of the bicarbonate, a strong acid be present, the products consist solely of hydrocyanic acid, hydrobromic acid, and a salt of formamidine disulphide, together with a trace of sulphuric acid.

When the components are mixed in simple aqueous solution all the products named above are formed.

According to a recent hypothesis (Dixon and Taylor, T., 1912, 101, 2502) it is supposed that in certain reactions of thiocarbamide the production of isothiocarbamide derivatives is brought about by the primary formation of additive compounds, resulting through the development of quadrivalence on the part of the sulphur atom, and the subsequent decomposition of the substances thus produced; for example:

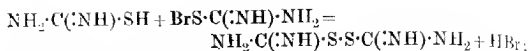


A strongly ionised acid, HX, could, in like manner, become united with the sulphur atom to yield a compound,  $\text{C}(\text{NH}_2)_2\cdot\text{SHX}$ , readily transformable into the basic form,  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{SH}$ , unstable by itself, but capable of retaining this configuration so long as it remains associated with a strong acid; and whilst the molecule is in this condition an oxidising agent, incapable of attacking the comparatively stable amino-group, could attack the SH-hydrogen. On the withdrawal of the combined acid the hydrogen at the SH-group, migrating, like an acyl radicle, to the imidic nitrogen, thiocarbamide would be regenerated.

There is reason to believe that such reversion occurs; for, in the reaction with cyanogen bromide, if the acidified solution of thiocarbamide is neutralised with sodium hydrogen carbonate, and then treated with the bromide, the products are the same as when the preliminary treatment with acid is omitted.

The mechanism of these reactions is explained as follows: where no acid is present, or allowed to become free, the thiocarbamide unites primarily with the whole molecule of cyanogen bromide; the elimination of the elements of hydrogen bromide from  $(\text{NH}_2)_2\text{C}:\text{S}:\text{CN}\cdot\text{Br}$  produces  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CN}$ , the residue decomposing (like certain alkylisothiocarbamides) into cyanamide and thiocyanic acid (thiocyanic acid or cyanogen hydrogen sulphide being the analogue of alkyl hydrogen sulphide).

When the interaction takes place in presence of a strong acid the primary union between the isothiocarbamide salt and the cyanogen bromide (as in the case of hydrogen sulphide) occurs at the SH-group, with formation of  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{C}\cdot\text{S}\cdot\text{C}(\text{NH})\cdot\text{NBr}$ . This decomposes into hydrogen cyanide and  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{Br}$ , the latter of which, attacking another molecule of isothiocarbamide salt, yields hydrogen bromide and formamidine disulphide:



thus, the non-production of thiocyanic acid is accounted for, as well as the production of all the substances detected in the reaction, save the trace of sulphuric acid. This last, no doubt, proceeds from the formamidine disulphide, which, as Werner has shown (T., 1912, 101, 2182), is very easily oxidised.

The reaction with thiocarbamide in presence of acid is essentially parallel to that with cyanogen bromide and thiosulphate already mentioned. At all events, the explanation is similar for both; in each case an additive compound is formed; both decompose, giving cyanide and an unstable residue containing  $\cdot\text{SBr}$ ; and in each case that residue combines with another molecule of the original thiocompound, eliminating hydrogen (or sodium) bromide.

The results when the interaction takes place in simple aqueous solution are now easily interpreted. At first, cyanamide is formed, together with hydrobromic and thiocyanic acids; these, combining with the yet unchanged thiocarbamide, and so producing *isothio*-carbamide salt, render possible the formation of hydrogen cyanide and formamidine disulphide.

#### *The Constitution of Cyanogen.*

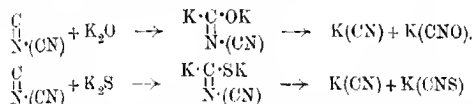
To cyanogen the constitution usually assigned is  $\text{N}\equiv\text{C}\cdot\text{C}\equiv\text{N}$ , the chief grounds for this formula being that the substance is producible from oxamide or from glyoxime, and that, when treated with hydrochloric acid, it yields oxamide.

On the other hand, when passed into cold aqueous alkali hydroxide it decomposes, forming alkali cyanide and alkali cyanate; in ordinary circumstances such behaviour would be used as an argument to show that the two carbon atoms are not singly linked. Moreover, when kept in aqueous solution, cyanogen yields not merely oxalic acid, but also hydrocyanic acid and ammonium carbonate; it may be recalled, too, that hydrocyanic acid, under the same conditions, yields some oxalic acid.

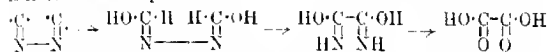
Further, although the methods of formation named above are consistent with the view that cyanogen is a normal, rather than an *iso*-compound, other methods of preparation are known, which do not suggest a normal constitution for the product; for example, silver cyanide or mercuric cyanide when heated yields cyanogen; there is considerable reason to believe that these are *isocyanides*, and hence (unless transformation is effected by the heating) the constitution of the resultant molecule is quite as likely to be  $\text{C}\cdot\text{N}\cdot\text{N}\cdot\text{C}$  as to be  $\text{N}\equiv\text{C}\cdot\text{C}\equiv\text{N}$ . Besides, the compound is producible

without strong heating, namely, through the decomposition of cupric *isocyanide*. It may, perhaps, be objected that it is not certain that the cupric salt is an *isocyanide*; but cyanogen bromide (which certainly is not  $\text{Br}\cdot\text{C}\cdot\text{N}$ ), when treated with cold aqueous potassium cyanide (probably  $\text{K}\cdot\text{N}\cdot\text{C}\cdot$ ), is said to yield ordinary cyanogen.

Further, the reaction with alkali hydroxide or with alkali sulphide so closely resembles that of cyanogen bromide with the same materials as to suggest that, in the case of cyanogen itself, one cyanogen radicle plays towards the other the same part as the halogen radicle in the bromide; in which case the changes may be explained on precisely similar lines, thus:



There is no special difficulty in accounting for the slow production of oxalic acid (or oxamide) from aqueous cyanogen, supposing it to be an *iso*-compound:



or for that of hydrocyanic acid and ammonium carbonate, for here water (of course, very slowly) may behave like alkali hydroxide (see above), the resultant cyanic acid decomposing into ammonia and carbon dioxide.

Another point seems worth notice. By the dehydration of an amide of the type  $\text{R}\cdot\text{CO}\cdot\text{NH}_2$ , the system  $\text{R}\cdot\text{C}\cdot\text{N}$ , presumably occurs; here the free valencies, if they are to link up, must necessarily do so between the carbon and the nitrogen; the product, therefore (apart from molecular rearrangement), must be  $\text{R}\cdot\text{C}\cdot\text{N}$ . In the dehydration of oxamide, however, this condition no longer holds; if two molecules of water are eliminated, the residue for the moment is  $\begin{array}{c} \cdot\text{C}\cdot\text{N}\cdot \\ \parallel \quad \parallel \\ \text{C}\cdot\text{N}\cdot \end{array}$ ; so that —unless it be assumed that the carbon valencies are incapable of uniting with one another—the system  $\begin{array}{c} \text{C}\cdot\text{N} \\ \parallel \quad \parallel \\ \text{C}\cdot\text{N} \end{array}$  would represent that proceeding from the most equable distribution of the four pairs of temporarily free valencies. Such a compound, breaking, according to circumstances, either at the doubly-linked carbon or at the singly-linked nitrogen pair of atoms, could yield all the products directly obtainable from cyanogen; thus, alkali hydroxide, by rupturing the double bond, could yield

those compounds the genesis of which is not easily intelligible on the assumption that the carbon atoms are but singly linked; whilst hydrochloric acid, attacking preferably the nitrogen atoms, might readily cause a hydrolysis which would leave the carbon atoms in single linking.

This formula, too, meets to some extent at least the difficulty as to the production of ordinary cyanogen from isocyanogen radicles; for, by the union of the two pairs of unsaturated carbon valencies, a cyclic compound could originate:



The constitution here suggested as best according with the properties of cyanogen is so far similar to that of Gutmann for cyanogen bromide, namely,  $\begin{array}{c} \text{C} \\ \text{N} \end{array} \gg \text{Br}$ , that, in the former, a tervalent group

(CN) replaces the tervalent halogen of the latter, thus:  $\begin{array}{c} \text{C} \\ \text{N} \end{array} \gg (\text{CN})$ .

Chattaway and Wadmore's formula for cyanogen bromide does not really conflict with that of Gutmann (*loc. cit.*), for the feeble extra valencies of the tervalent haloid element would very readily be broken, the carbon valencies thus becoming "free," and hence able to manifest the unsaturated character peculiar to the molecule, including its poisonousness. In like manner the cyanogen molecule, assisted, perhaps, by its own internal strains, could easily open out into a compound,  $\text{:C}\cdot\text{N}\cdot\text{N}\cdot\text{C}\cdot$ , the poisonousness of which might well be anticipated.

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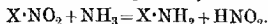
### CH.—Derivatives of *o*-Xylene. Part III. The Presence of a Mobile Nitro-group in Each of the Two Trinitro-*o*-xylenes.

By ARTHUR WILLIAM CROSSLEY and WALTER RILEY PRATT.

In a paper communicated to the Society in 1911 (T., 99, 2345) reference was made to the action of alcoholic ammonia on the trinitro-*o*-xylenes, when a nitro-group is replaced by an amino-group, as reduction. In the discussion which followed the reading of the paper, Prof. Morgan (P., 1911, 27, 308) pointed out that this was not reduction in the accepted sense of the word, but probably a simple replacement of a mobile nitro-group, and shortly afterwards Prof. Meldola called the attention of the authors to the

same point, instancing the behaviour of 2:3:5-trinitro-4-acetyl-aminophenol (T., 1908, 93, 1659) under similar conditions.

Further investigation has proved that such is, as a matter of fact, the case, a nitro-group in each of the two trinitro-*o*-xylenes being replaced readily, not only by the amino-group, but by a variety of substituted amino-groups. The reactions take place with liberation of nitrous acid, as exemplified by the following expression:



The odour of nitrous acid was noticeable on evaporation of many of the reaction solutions, and, in one case, the interaction of 3:4:6-trinitro-*o*-xylene and benzylamine, crystals of benzylamine nitrite were actually isolated.

Derivatives have been prepared using the following primary amines: methylamine, ethylamine, aniline, *p*-toluidine, *o*- and *p*-anisidine, benzylamine, and with the secondary amines, dimethylamine and piperidine.

Neither 3:4:5-trinitro- nor 3:4:6-trinitro-*o*-xylene reacts with *o*- or *m*-nitroaniline or methylaniline, and although interaction takes place between both trinitro-*o*-xylenes and (*a*) diethylamine, (*b*) *p*-phenylenediamine with formation of deep coloured solutions and resinous products, no crystalline substances could be isolated. The same remark applies to 3:4:5-trinitro-*o*-xylene and *o*-toluidine, but from the latter substance and 3:4:6-trinitro-*o*-xylene a small amount of crystals was isolated, melting at 139°.

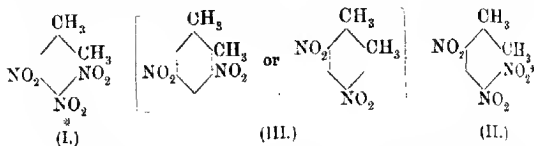
As pointed out by Meldola (*ibid.*, p. 1667), the influence of an ortho-substituent in these reactions is noted in the relative non-activity of *o*-nitroaniline and *o*-toluidine, although *o*-anisidine is decidedly reactive; but whereas Meldola obtained products with *m*-nitroaniline, this substance, as stated above, has been found to give negative results with the trinitro-*o*-xylenes.

The reactions were, as a rule, carried out by adding slightly more than the calculated amount of the amine to a cold alcoholic suspension of the trinitro-*o*-xylene, and allowing the mixture to remain. In other cases the solution was heated for lengths of time varying from ten minutes to three hours, and solvents other than alcohol, for example, ether and benzene, were employed. The excess of amine was, in most cases, removed by washing with dilute hydrochloric acid, in which solvent the amino-products are practically insoluble.

There are marked differences in the rates at which the various reactions take place as indicated in some cases in the experimental portion of this paper; for example, 3:5-dinitro-4-benzylamino-*o*-xylene is formed almost immediately on adding benzylamine to 3:4:5-trinitro-*o*-xylene, although the latter is only suspended in

alcohol, whereas the reaction with aniline, under similar conditions, is not complete in fourteen days. Many experimental difficulties will, however, have to be overcome before any quantitative measurements of value can be given, and in many cases the difficulties appear to be insurmountable.

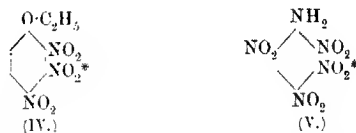
The constitutions of the two trinitro-*o*-xylenes are represented by formulae I and II, and there can be no doubt as to which of the



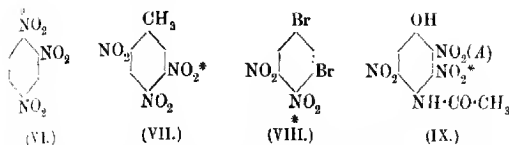
nitro-groups is the active one (marked \*) in each case, for when the products of the action of ammonia on these substances are diazotised and the diazo-group removed by boiling with alcohol, they both yield 3:5-(4:6)dinitro-*o*-xylene (III).

It would appear to be an established fact that in order to exhibit mobility a nitro-group must be situated in an ortho-position, and in certain cases also para- with respect to some acid radicle present in the nucleus (compare Hepp, *Annalen*, 1882, **215**, 362, 364; Staedel and Kolb, *ibid.*, 1890, **259**, 208, 220, 224; Laubenheimer, *Ber.*, 1876, **9**, 1826, 1828; 1878, **11**, 1156, 1159; Nietzki, *Ber.*, 1878, **11**, 1448; Flürscheim, *P.*, 1910, **26**, 81; Meldola and Eyre, *T.*, 1901, **79**, 1676; 1902, **81**, 988; Meldola, *T.*, 1906, **89**, 1935; 1908, **93**, 1659; Blanksma, *Rec. trav. chim.*, 1908, **27**, 42, 49).

In 3:4:5-trinitro-*o*-xylene the mobile group is ortho with regard to two other nitro-groups, corresponding exactly with the position of the active group (marked \*) in 2:3:4-trinitrophenetole (IV) (Blanksma, *loc. cit.*, p. 50), and also in tetranitroaniline (V) (Flürscheim):



In 2:4:6-trinitro-*o*-xylene the mobile group is situated ortho and para to the other acidic groups, a position which seems perhaps to be the most favourable for the change to take place, as evidenced by trinitrobenzene (VI); trinitrotoluene (VII) (Hepp, *loc. cit.*, 361, 364); tetranitroaniline (V) (Flürscheim); and dibromodinitrobenzene (VIII) (Blanksma, *loc. cit.*, 43):



It is, however, of interest to note that although Meldola's trinitroacetylaminophenol (IX) contains a nitro-group (1) situated ortho and para to two other nitro-groups, it is not this group but the one in position 3 (\*) which is mobile. Evidently in this case mobility must be to some extent influenced by the other groups present in the molecule.†

As other derivatives of *o*-xylene have been encountered which appear to contain mobile groups, the investigation is being continued more particularly with regard to the relative rates at which the mobile nitro-groups are replaced.

#### EXPERIMENTAL.

##### *Derivatives of 3:4:5-Trinitro-o-xylene.*

3:5-Dinitro-*o*-4-*xy*lidine (3:5-dinitro-4-amino-*o*-xylene)  
(T., 1911, 99, 2350).

3:5-Dinitro-4-methylamino-*o*-xylene, prepared from methylamine and trinitro-*o*-xylene in alcoholic solution in the cold, crystallises from alcohol, in which solvent it is very sparingly soluble, in stout, scarlet plates, melting at 143°:

0.1058 gave 16.8 c.c.  $N_2$  (moist) at 17° and 759 mm.  $N = 18.67$ .

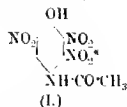
$C_9H_9O_4N_3$  requires  $N = 18.66$  per cent.

3:5-Dinitro-4-dimethylamino-*o*-xylene is obtained, in nearly theoretical amount, by heating the trinitro-*o*-xylene for ten minutes with dimethylamine in alcoholic solution. It crystallises from alcohol in orange-red needles, melting at 103–104°:

0.1104 gave 16.6 c.c.  $N_2$  (moist) at 16° and 762 mm.  $N = 17.81$ .

$C_{10}H_{13}O_4N_3$  requires  $N = 17.57$  per cent.

† Since the above paper was written, Professor Meldola has kindly communicated to the authors that further work has shown that the trinitroacetylaminophenol described by him has the nitro-groups in the 2:3:6-positions and not 2:3:5, as previously stated (compare T., 1913, 103, 877). The latter substance has recently been prepared and will shortly be described:



It will, therefore, be noted that the mobile group in 2:3:6-trinitroacetylaminophenol (I) is again situated ortho and para to the other two nitro-groups in the molecule.



3: 5-Dinitro-4-ethylamino-o-xylene, prepared by heating trinitro-o-xylene with excess of ethylamine in alcoholic solution for three hours (yield almost theoretical), is readily soluble in chloroform or benzene, and crystallises from alcohol in orange needles, melting at 115°:

0.1536 gave 23.2 c.c.  $N_2$  (moist) at 14° and 748 mm.  $N = 17.69$ .  
 $C_{10}H_{13}O_4N_3$  requires  $N = 17.57$  per cent.

3: 5-Dinitro-4-anilino-o-xylene.—Trinitro-o-xylene was suspended in alcohol, and excess of aniline added, when, on standing, the nitro-compound slowly passed into solution, and red crystals separated. The reaction was not, however, ended after fourteen days, but in ethereal solution it was complete in three days. Dinitroanilinoxylene crystallises from alcohol in orange-red needles, melting at 134°:

0.1318 gave 16 c.c.  $N_2$  (moist) at 15° and 770 mm.  $N = 14.58$ .  
 $C_{14}H_{13}O_4N_3$  requires  $N = 14.63$  per cent.

3: 5-Dinitro-4-p-toluidino-o-xylene was prepared from the trinitro-o-xylene and *p*-toluidine in alcoholic solution on gentle warming. Prolonged heating causes the formation of large quantities of resinous substances. It crystallises from alcohol in fine, orange needles, melting at 133°:

0.1120 gave 13.2 c.c.  $N_2$  (moist) at 10° and 766 mm.  $N = 13.98$ .  
 $C_{12}H_{13}O_4N_3$  requires  $N = 13.99$  per cent.

3: 5-Dinitro-4-o-anisidino-o-xylene is obtained, in theoretical amount, by allowing trinitroxylene and *o*-anisidine to remain in alcoholic solution for seven days. It crystallises from alcohol in stout, crimson-lake needles, melting at 138–139°:

0.1500 gave 16.8 c.c.  $N_2$  (moist) at 10° and 753 mm.  $N = 13.38$ .  
 $C_{15}H_{13}O_5N_3$  requires  $N = 13.24$  per cent.

3: 5-Dinitro-4-p-anisidino-o-xylene crystallises from alcohol in bright crimson needles, melting at 131°:

0.1454 gave 16.6 c.c.  $N_2$  (moist) at 19° and 762 mm.  $N = 13.38$ .  
 $C_{15}H_{13}O_5N_3$  requires  $N = 13.24$  per cent.

The reaction with *p*-anisidine is complete in three days in ethereal solution.

3: 5-Dinitro-4-benzylamino-o-xylene is formed in almost theoretical quantity in a very short time after adding excess of benzylamine to an alcoholic suspension of trinitro-o-xylene. It is readily soluble in ether, chloroform, benzene, or acetone, but only sparingly so in alcohol, from which solvent it crystallises in glistening, orange plates, melting at 128.5°:

0.1164 gave 13.6 c.c.  $N_2$  (moist) at 17° and 775 mm.  $N = 14.07$ .  
 $C_{12}H_{15}O_4N_3$  requires  $N = 13.99$  per cent.

3: 5-Dinitro-4-piperidino-o-xylene is obtained in 90 per cent. of

the theoretical amount by heating the trinitro-*o*-xylene with excess of piperidine for two hours in benzene solution. It crystallises from alcohol in bright, orange-red needles, melting at 137—138°:

0.139 gave 14.8 c.c.  $N_2$  (moist) at 16° and 752 mm.  $N = 15.18$ .  
 $C_{13}H_{17}O_4N_3$  requires  $N = 15.05$  per cent.

*Derivatives of 3:4:6-Trinitro-o-xylene.*

4:6-Dinitro-*o*-3-xylydine (4:6-dinitro-3-amino-*o*-xylene,  
 T., 1911, 99, 2348).

4:6-Dinitro-3-methylamino-*o*-xylene is prepared by suspending trinitro-*o*-xylene in alcohol and adding excess of a 30 per cent. solution of methylamine in alcohol. A green colour is first produced, changing to blue, red, and finally yellow, with deposition of yellow crystals (theoretical amount). It crystallises from alcohol in orange needles, melting at 90—91°:

0.0341 gave 15.5 c.c.  $N_2$  (moist) at 20° and 755 mm.  $N = 18.96$ .  
 $C_9H_{11}O_4N_3$  requires  $N = 18.66$  per cent.

4:6-Dinitro-3-dimethylamino-*o*-xylene.—On adding an alcoholic solution of dimethylamine to trinitroxylene suspended in alcohol, a green colour is immediately developed, which changes to blue, purple, red, and finally yellow, with deposition of solid. When the mixture is heated on a water-bath the yellow stage is reached in ten minutes. The solid crystallises from alcohol in orange needles, melting at 91—92°:

0.1074 gave 16.4 c.c.  $N_2$  (moist) at 18° and 756 mm.  $N = 17.82$ .  
 $C_{10}H_{13}O_4N_3$  requires  $N = 17.57$  per cent.

4:6-Dinitro-3-ethylamino-*o*-xylene.—When an alcoholic solution of ethylamine is added to a suspension of trinitro-*o*-xylene in alcohol, heat is evolved, a yellow colour develops, and a yellow solid is deposited (yield theoretical). It crystallises from alcohol in short, orange needles, melting at 75—76°:

0.1288 gave 19.4 c.c.  $N_2$  (moist) at 15° and 748 mm.  $N = 17.57$ .  
 $C_{10}H_{13}O_4N_3$  requires  $N = 17.57$  per cent.

4:6-Dinitro-3-anilino-*o*-xylene.—Trinitro-*o*-xylene is suspended in absolute alcohol, and three times the calculated quantity of aniline added. A red colour at once develops, and after forty-eight hours all the trinitro-compound disappears and is replaced by red plates. The reaction is accelerated by heat, but resinous substances are also formed, whereas by carrying it out in ether and evaporating the ether without the aid of heat, a theoretical amount of the substance is obtained.

Dinitroanilinoxylene is very soluble in chloroform, ether, benzene,

or acetone, but only sparingly so in light petroleum, and crystallises from alcohol in bright red plates, melting at  $137^{\circ}$ :

0.1350 gave 17 c.c.  $N_2$  (moist) at  $16^{\circ}$  and 758 mm.  $N = 14.79$ .

$C_{14}H_{13}O_4N_3$  requires  $N = 14.63$  per cent.

4: 6-Dinitro-3-*p*-toluidino-o-xylene.—Trinitroxylene, mixed with dry, powdered *p*-toluidine, develops a red colour, and a deep red solution is formed on addition of alcohol. After twelve hours a quantity of red crystals separate, representing 70 per cent. of the theoretical amount. The change takes place more rapidly on heating, but resinous substances are also formed.

Dinitro-*p*-toluidinoxylene crystallises from alcohol in orange-red plates, melting at  $111^{\circ}$ :

0.1316 gave 15.6 c.c.  $N_2$  (moist) at  $14^{\circ}$  and 766 mm.  $N = 14.22$ .

$C_{15}H_{13}O_4N_3$  requires  $N = 13.99$  per cent.

4: 6-Dinitro-3-*o*-anisidino-o-xylene, prepared in alcoholic solution, crystallises from alcohol in brick red needles, melting at  $126-127^{\circ}$ :

0.1645 gave 18.6 c.c.  $N_2$  (moist) at  $13^{\circ}$  and 758 mm.  $N = 13.46$ .

$C_{15}H_{13}O_4N_3$  requires  $N = 13.24$  per cent.

4: 6-Dinitro-3-*p*-anisidino-o-xylene crystallises from alcohol in garnet-coloured, flattened needles, melting at  $118^{\circ}$ . The reaction between *p*-anisidine and trinitroxylene is complete in ethereal solution after forty-eight hours:

0.1356 gave 15.4 c.c.  $N_2$  (moist) at  $14^{\circ}$  and 758 mm.  $N = 13.47$ .

$C_{15}H_{13}O_4N_3$  requires  $N = 13.24$  per cent.

4: 6-Dinitro-3-benzylamino-o-xylene.—When benzylamine is added to a benzene solution of trinitroxylene, a yellow colour is formed and heat evolved. On cooling, crystals of benzylamine nitrite separate. The whole is heated on a water-bath for three hours, and after working up in the usual way the resulting oil slowly solidifies. The solid is readily soluble in chloroform, benzene, or acetone, and crystallises from a mixture of chloroform and light petroleum (b.p.  $40-60^{\circ}$ ) in orange prisms, melting at  $59^{\circ}$ :

0.1868 gave 22 c.c.  $N_2$  (moist) at  $16^{\circ}$  and 763 mm.  $N = 13.97$ .

$C_{15}H_{13}O_4N_3$  requires  $N = 13.99$  per cent.

4: 6-Dinitro-3-piperidino-o-xylene crystallises from aqueous alcohol or aqueous acetone in orange plates, melting at  $98^{\circ}$ :

0.0938 gave 12.1 c.c.  $N_2$  (moist) at  $16^{\circ}$  and 752 mm.  $N = 15.07$ .

$C_{13}H_{17}O_4N_3$  requires  $N = 15.05$  per cent.

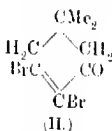
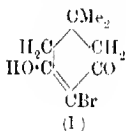
The reaction with piperidine is best carried out by heating in alcoholic solution for three hours.

III.—*Derivatives of o-Xylene. Part IV. Synthesis of 4 : 5-Dibromo-3-o-xenol.*

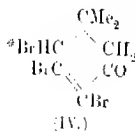
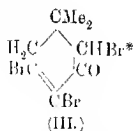
By ARTHUR WILLIAM CROSSLEY and SYDNEY SMITH.

IN 1903 Crossley and Le Sueur (T., **83**, 127) described a dibromoxenol melting at  $96.5^\circ$ , which was obtained from the product of the action of phosphorus pentabromide on dimethyldihydroresorcin. It was then suggested that this substance was a derivative of 3-o-xenol, because on further bromination it yielded a tribromoxenol melting at  $183^\circ$ . Tribromo-3-o-xenol melting at  $184^\circ$ . In the action of phosphorus pentabromide on dimethyldihydroresorcin, the main initial products are not bromoxenols, but are hydroaromatic in nature, the principal one isolated being tribromodimethylcyclohexenone (tribromoketodimethyltetrahydrobenzene) (III or IV).

Dibromodimethylcyclohexenone (II) results from the action of phosphorus tribromide on bromodimethyldihydroresorcin (I) (*loc.*



*op.*, p. 122), and its constitution would therefore appear to be beyond doubt. When treated with bromine, it is converted into tribromodimethylcyclohexenone, which may be represented by either of the two formulae III or IV, although the former appears to be the more likely.

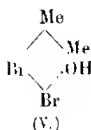


Recently (P., 1912, **28**, 333) the above-mentioned dibromoxenol has been obtained by the action of dilute alcoholic potassium hydroxide on tribromodimethylcyclohexenone. In this reaction, one bromine atom must be eliminated as hydrogen bromide, and this would almost certainly be the one marked \*, in which case its actual position in tribromodimethylcyclohexenone is of no moment to the present argument, but if this is the bromine atom to be removed then the position of the remaining bromine atoms

VOL. CIII.

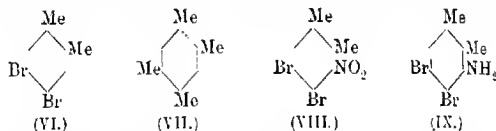
is fixed; (b) the ketonic group would become hydroxylic, thus determining the position of the hydroxyl group in the resulting dibromoxylene; (c) a methyl group must wander, and since on further bromination the resulting dibromoxylene has been proved to yield tribromo-3-*o*-xylene, the positions of the methyl groups relative to the hydroxyl group become evident.

Assuming this argument to be correct, only one possibility exists for the constitution of the dibromoxylene melting at 96.5°, namely, 4:5-dibromo-3-*o*-xylene (V), and this supposition has now been



proved to be correct by the synthesis of a substance of this constitution, which proves to be identical with the dibromoxylene obtained by the action of phosphorus pentabromide on dimethyl-dihydroresorcin.

Jacobson (*Ber.*, 1884, **17**, 2377) has shown that when *o*-xylene is brominated in the presence of iodine, two dibromo-*o*-xylenes are produced, the one a liquid, the other a solid, melting at 88°. That the latter is 4:5-dibromo-*o*-xylene (VI) was proved by the fact that



on treatment with sodium and methyl iodide, it gave durene (1:2:4:5-tetramethylbenzene, VII). When 4:5-dibromo-*o*-xylene is nitrated, it yields a dibromonitro-*o*-xylene, and as the molecule is symmetrical, this can only be 4:5-dibromo-3-nitro-*o*-xylene (VIII), which on reduction is converted into 4:5-dibromo-3-amino-*o*-xylene (IX). In this latter substance the amino-group can be replaced by hydroxyl through the agency of the diazo reaction, and there results 4:5-dibromo-3-*o*-xylene.

#### EXPERIMENTAL.

4:5-Dibromo-*o*-xylene (Jacobson, *loc. cit.*) was prepared from quantities of 10 grams of *o*-xylene, 0.4 gram of iodine, and 31 grams of bromine. The whole, after dissolving in ether, washing with potassium hydroxide solution, water, drying and evaporating the ether, weighed 24–25 grams, and was semi-solid. The amount of

pure dibromo-*o*-xylene obtained after crystallisation from alcohol was 11.5 grams, melting at  $87-88^{\circ}$ .

Dibromo-*o*-xylene (compare Tohl, *Ber.*, 1885, **18**, 2562) in quantities of 10 grams was warmed on the water-bath for one hour, and frequently shaken with 25 c.c. of a mixture of 3 volumes of fuming nitric acid and 1 volume of glacial acetic acid. After pouring into water and recrystallising from alcohol, 8 grams of 4:5-dibromo-3-nitro-*o*-xylene, melting at  $143-144^{\circ}$ , were obtained.

Dibromonitro-*o*-xylene was reduced in quantities of 5 grams at one time by heating for four hours with 15 grams of iron filings and 50 grams of glacial acetic acid. After steam distillation and crystallisation of the resulting solid from alcohol, 2 to 2.4 grams of 4:5-dibromo-3-*o*-xylidine, melting at  $103^{\circ}$ , were isolated.

4:5-Dibromo-3-*o*-xylidine was diazotised by suspending 5 grams in 75 c.c. of 40 per cent. sulphuric acid, and, while maintaining the temperature at  $50-60^{\circ}$ , gradually adding a 20 per cent. solution of sodium nitrite until a reaction was shown to starch-iodide paper. The whole was then poured into 125 c.c. of 40 per cent. sulphuric acid, heated to near the boiling point, and after some time was distilled in a current of steam, when a white solid passed over. The distillate was rendered alkaline with sodium hydroxide, filtered from a slight amount of insoluble matter, acidified, and the precipitated dibromoxyleneol crystallised from dilute alcohol (yield, 2.8 to 3.5 grams):

0.1230 gave 0.1663 AgBr. Br = 57.52.

$C_8H_5OBr_2$  requires Br = 57.14 per cent.

4:5-Dibromo-3-*o*-xyleneol is insoluble in sodium carbonate solution, readily soluble in the cold in potassium hydroxide solution, chloroform, acetone, benzene, or ether, and crystallises from aqueous alcohol in long, glistening, flattened needles, melting at  $97^{\circ}$ . When treated with bromine in chloroform solution, it is converted into 4:5:6-tribromo-3-*o*-xyleneol, melting at  $185^{\circ}$ .

The *acetyl* derivative was prepared by heating the xyleneol with a mixture of acetyl chloride and acetic anhydride. It is readily soluble in the cold in acetone, ethyl acetate, chloroform, or benzene, somewhat less readily so in alcohol, and crystallises from light petroleum (b. p.  $40-60^{\circ}$ ) in large, hexagonal prisms, melting at  $78^{\circ}$ :

0.1103 gave 0.1296 AgBr. Br = 49.99.

$C_{11}H_{10}O_2Br_2$  requires Br = 49.69 per cent.

The *benzoyl* derivative, prepared in the usual manner, crystallises from alcohol in small, transparent rhombs, melting at  $153^{\circ}$ :

0.1116 gave 0.1100 AgBr. Br = 41.93.

$C_{15}H_{12}O_2Br_2$  requires Br = 41.67 per cent.

It is readily soluble in the cold in chloroform, somewhat less so in cold ethyl acetate or benzene, and readily soluble in acetone on warming.

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#### (IV).—*The Behaviour of Calcium and Magnesium Salts with Soap Solutions and the Determination of Hardness of Water.*

By HELEN MASTERS and HENRY LLEWELLYN SMITH.

MANY observers have noted the difference in behaviour of magnesium and calcium salts when titrating waters with soap solutions for the determination of "hardness," and the difficulty of obtaining a satisfactory end-point in the presence of magnesium salts has become well known.

The work described below was undertaken with the object of tracing the cause of this difference and determining more satisfactory conditions.

Buchner (*Chem. Zeit.*, 1892, **16**, 1854) states that temperature exerts a great influence on the appearance of the lather. The thick foam which remains five minutes after the precipitation of calcium and magnesium salts at 15° remains constant for hardly a minute at the higher temperatures reached in midsummer, and scarcely longer with a further addition of soap.

Teed (*J. Soc. Chem. Ind.*, 1889, **8**, 256) states that calcium salts require  $1\frac{1}{2}$  and magnesium salts  $1\frac{1}{2}$  times the equivalent of soap for the production of a permanent lather.

Winkler (*Zeitsch. anal. Chem.*, 1901, **40**, 82) states that magnesium salts require more soap than an equivalent amount of calcium salts, potassium oleate being the soap used.

Jackson (*Chem. News*, 1884, **49**, 149), using Castile soap solution, found that when the hardness due to calcium salts exceeded six degrees, no evidence could be obtained of magnesium salts unless present in amount exceeding 10 per cent. of the calcium salts. He suggested heating to 70° to obtain more accurate results.

The standard soap solutions used in the work here described were made from various soaps, and the results indicate that soaps made from the saturated fatty acids give more accurate results than those

derived from unsaturated acids. As, however, sodium oleate makes a convenient and stable solution, its behaviour was further investigated. The solubility of calcium and magnesium oleates and the nature of the precipitate obtained on titration seemed worth investigating.

Standard solutions of calcium and magnesium salts were titrated with aqueous-alcoholic solutions of sodium oleate, potassium palmitate, Castile soap, and potassium myristate. The soap solutions (with the exception of Castile soap) were prepared by dissolving the acid in alcohol, neutralising with sodium or potassium hydroxides, and diluting with water and alcohol, so that the finished solution contained 50 per cent. of alcohol. They were standardised, so that 100 c.c. water containing 10 milligrams of calcium carbonate required 11 c.c. of soap solution.

The molecular weights of the acids were determined by titration with alkali in alcoholic solution. The iodine absorption was determined by means of Hanus' solution.

The following results were obtained:

Myristic acid, M.W. 228; iodine absorption, 0.5 per cent.; m. p. 33.3°.

Palmitic acid, M.W. 257.7; iodine absorption, 0.8 per cent.; m. p. 61.5–62°.

Oleic acid, M.W. 283; iodine absorption, 87.4 per cent., corresponding with 97 per cent. of oleic acid; the refractive index was 1.4542 at 40°.

The Castile soap gave a clear neutral solution in alcohol. The fatty acids had a mean molecular weight of 280.9, and melted at 23°. They absorbed 46.1 per cent. of iodine, corresponding with 52 per cent. of unsaturated acids in terms of oleic acid. Refractive index 1.4493 at 40°. As will be seen, a mixture of potassium myristate and sodium oleate standard solutions in equal volumes gives the same results as the solution of Castile soap when used to titrate calcium and magnesium salts.

All the titrations were done on 100 c.c. of water containing calcium or magnesium salts, separately or together, equivalent to 10 milligrams of calcium carbonate.

The figures on p. 991 are the mean of a large number of closely agreeing titrations.

Titrations with sodium oleate and magnesium salts were carried out at temperatures ranging from 15° to 60°, and the following results obtained. At temperatures up to 30°, 13 c.c. of sodium oleate were required, whilst above 40° only 8 c.c. were necessary. The change between these two temperatures seems somewhat sudden; at 35°, 11–12 c.c. were required. The difficulty of keeping the



temperature constant while titrating and shaking, and of obtaining a sharp end-point, prevented a more accurate determination.

Soap solution used.	Equivalent (in milligrams of $\text{CaCO}_3$ ) of the salts contained in 100 c.c. of solution.		C.c. of soap solution required	
	$\text{CaCl}_2$	$\text{MgCl}_2$	at 15°.	at 60°.
Sodium oleate .....	10	—	11.0	12–12.5
.....	—	10	13.0	8.0
Potassium palmitate .....	10	—	11.0	10–11
.....	—	10	11.0	9.0
Castile soap .....	10	—	11.0	12.0
.....	—	10	12.5	8.0
Myristate and oleate .....	10	—	11.0	—
(equal volumes) .....	—	10	12.5	—
Potassium myristate .....	10	—	11.0	10.5–11.0
.....	—	10	11.0	10.5–11.0

The results in the table given above show the difference in behaviour of soaps made from saturated and unsaturated fatty acids when used for titrating calcium and magnesium salts.

With palmitate and myristate, the end-point, whilst sharp at the ordinary temperature, became unsatisfactory at 60°.

The lather obtained from sodium oleate and calcium chloride was more lasting at 15° than at 60°, whilst with magnesium chloride a white froth was formed early at 60°, which made the true lather difficult to distinguish.

With water and sodium oleate alone, a more profuse lather was obtained at the higher temperature.

The potassium palmitate solution was unsatisfactory, as except in the warmest weather a considerable precipitate formed even after keeping for twenty-four hours and filtering. The precipitate, on analysis, proved to be potassium hydrogen palmitate. Increasing the quantity of alcohol to 75 per cent. prevented this to some extent, but not sufficiently to make it stable.

Potassium myristate gave a clear solution which was quite as stable as that of sodium oleate, and when standardised with calcium chloride gave accurate results with magnesium salts and with mixtures of calcium and magnesium salts in all proportions.

When potassium palmitate was used for titrating magnesium salts, it was noted that after the addition of about half the soap the magnesium palmitate appeared as a flocculent precipitate suspended in a clear liquid. As the titration was completed the precipitate was rapidly dispersed, and at the end the liquid was uniformly cloudy, and no sedimentation took place until after some minutes. The same kind of separation took place when potassium myristate was used, but it was not so marked. With sodium oleate no such separation was noticed.

This observation is of interest as showing possibly some analogy to the coagulation of colloids by salts of metals of different valency, the magnesium sulphate having a greater effect than the sodium sulphate finally present.

With waters containing both calcium and magnesium salts, accurate results could only be obtained with soaps made from saturated fatty acids. With sodium oleate the end-points were unsatisfactory. When the calcium salts present exceeded 70 per cent. of the total hardness, and the titration was performed rapidly, a lather was obtained when rather more than the equivalent of the calcium alone was added. On keeping, the titration could be continued, but not with much accuracy, and the total amount of soap used was less than required by theory. This was the case at all temperatures with mixtures varying from 10 per cent. of magnesium and 90 per cent. of calcium to 90 per cent. of magnesium and 10 per cent. of calcium.

The equivalent of sodium oleate used in these experiments agrees closely with the figures given by Teed (*loc. cit.*).

One hundred c.c. of sodium oleate solution contained  $\text{Na}_2\text{O}$  equivalent to 25 c.c. of  $N/10$ -hydrochloric acid, giving 0.760 sodium oleate in 100 c.c. of solution.

Ten milligrams of calcium carbonate (equivalent to 60.8 milligrams of sodium oleate) required 83.6 milligrams, or 1.37 times the equivalent of oleate.

An equivalent amount of magnesium salts required 98.8 milligrams of sodium oleate, or 1.62 times the equivalent.

It was noted, however, that at 60° the magnesium salts used up 60 milligrams only or practically the equivalent.

Some of the solutions titrated with sodium oleate were kept for some time. Those containing calcium salts remained translucent, with hardly any formation of precipitate, but on heating to 60° they became opaque, and particles separated. In the case of magnesium salts, an opaque mixture with considerable precipitate formed after a short time at 15°. On heating to 60°, the mixture did not clear, but the particles became suspended, and there was but little sediment. Attempts were made to separate this suspended matter by centrifugalising for fifteen to twenty minutes at 2,000 revolutions per minute. With calcium salts no separation occurred. With magnesium salts a fair separation was effected. Magnesium sulphate equivalent to 10 milligrams of calcium carbonate was used with 6 c.c. to 15 c.c. of sodium oleate solution in a total volume of 100 c.c. With 15 c.c. of oleate, but little separation occurred. In all cases the clearer supernatant liquid contained magnesium, and was alkaline to methyl-orange.

The precipitate from a number of experiments (using 10 c.c. of sodium oleate solution) was collected and dried in a vacuum over sulphuric acid, after pressing on a porous plate. Analysis showed it to be normal magnesium oleate with a small quantity of sodium salt. (Found,  $\text{MgO} = 6.46$ . Calc.,  $\text{MgO} = 6.83$  per cent.)

A few mixtures were placed in the centrifuge at  $60-80^\circ$ , but no separation occurred at this temperature.

In the case of titrations carried out with soaps obtained from saturated fatty acids, separation occurred with both calcium and magnesium salts on keeping.

From the behaviour of sodium oleate with calcium and magnesium salts, it appeared likely that the solubilities of the oleates had some influence on the results. They were determined at  $15^\circ$  and  $60^\circ$ , upward filtration being employed through a layer of filter paper and muslin over the end of a tube  $\frac{3}{8}$  in. in diameter.

The salts were prepared by mixing excess of solutions of the chlorides with sodium oleate. They were purified by washing and drying in a vacuum over sulphuric acid, redissolving in light petroleum (in which they are freely soluble), filtering, and evaporating. Both salts were in a porous, granular condition, and tended to become moist and sticky on exposure to air, particularly the magnesium salt, which softens to a pasty mass in water above  $40^\circ$ .

These salts are not quite pure, some water and light petroleum finally remaining to the extent of about 5 per cent.

On analysis, the magnesium salt gave  $\text{MgO} = 6.4$ , and oleic acid = 91.65 per cent., or 1:14.13 (theory, 1:14.10). The calcium salt contained  $\text{CaO} = 8.87$  (theory, 9.30), corresponding with 95.3 per cent. of calcium oleate.

The quantities dissolving in water are so small that it was only possible to estimate the calcium and magnesium oxides (weighed as pyrophosphate). About 150 grams of solution were taken for the estimation. At the higher temperature,  $60^\circ$ , it was found necessary to redissolve the calcium oxide obtained by ignition, and reprecipitate as oxalate, as an appreciable amount of soluble matter was obtained from the glass vessel. The solutions were slightly turbid even after filtration, and were faintly alkaline to phenolphthalein.

Calcium and magnesium palmitate were prepared by mixing excess of a solution of the chloride with a solution of potassium palmitate. The precipitate was thoroughly washed until, on digestion with water and filtering, the filtrate gave no reaction for chloride.

The following figures were obtained, 100 grams of solution being used in each case:

Temperature.	Calcium oleate.	Magnesium oleate.	Calcium palmitate.	Magnesium palmitate.
15°	0.0041 CaO	0.0015 MgO	0.0030 CaO	0.0009 MgO
60	0.0023 CaO	0.0020 MgO to 0.0025	0.0032 CaO	0.0010 MgO

With both calcium and magnesium palmitate, temperature has no appreciable effect on the solubility, and neither solution gave a pink colour with phenolphthalein.

The solution of magnesium oleate in water at all temperatures gave a lather on shaking, like the false lather always obtained early in the titrations of magnesium salts.

That the separation of particles of magnesium oleate, previously mentioned, is the cause of more soap solution being required is shown by the following experiments. Magnesium oleate was added to 100 c.c. of water containing magnesium sulphate equivalent to 10 milligrams of calcium carbonate, and the mixture then titrated with sodium oleate solution:

MgSO <sub>4</sub> alone .....	13.9 c.c. sodium oleate required
MgSO <sub>4</sub> + 0.1 gram Mg oleate .....	15.5 c.c. " " "
MgSO <sub>4</sub> + 0.2 grams Mg oleate .....	17.0 c.c. " " "

At temperatures above 40°, the addition of magnesium oleate did not increase the amount of soap solution necessary to form a lather, and when the mixture was kept above this temperature for some time before titrating, the amount of soap solution then required to form a lather was slightly less than that required by the magnesium sulphate alone.

Similar experiments with calcium salts gave results in the reverse order, the addition of calcium oleate at 15° affecting the result but little:

CaCl <sub>2</sub> (= 10 mg. CaCO <sub>3</sub> ) alone...	11 c.c. sodium oleate required
CaCl <sub>2</sub> + 0.2 gram Ca oleate .....	11.5-12 c.c. sodium oleate required

At 60° the results were more like those obtained with magnesium salts at 15°, thus:

CaCl <sub>2</sub> (= 10 mg. CaCO <sub>3</sub> ) .....	12.0 c.c. sodium oleate required
CaCl <sub>2</sub> + 0.1 gram calcium oleate .....	15.5 c.c. " " "
CaCl <sub>2</sub> + 0.2 " " " .....	16.0-16.5 c.c. sodium oleate required

#### Conclusions.

It is impossible to obtain accurate measurements of hardness in water containing magnesium salts with a soap solution prepared with sodium oleate standardised with calcium salts.

This seems to be due to the fact that magnesium oleate is less soluble than calcium oleate at 15°, and particles of magnesium oleate separate and carry down or adsorb some sodium oleate. With mixtures of calcium and magnesium salts sodium oleate is unsatisfactory, accurate determination being impossible. Heating to higher temperatures up to 60° is of no advantage.

Soaps prepared with the saturated fatty acids are more satisfactory. Potassium myristate makes a stable soap solution, and gives accurate results with calcium and magnesium salts occurring alone or together.

Potassium palmitate solution deposits an acid soap, and is therefore unsuitable for use in the concentration necessary for these titrations.

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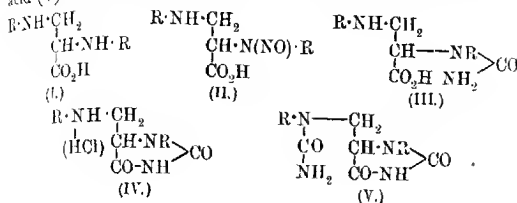
#### CV.—*Carbamido- and Other Derivatives of $\alpha\beta$ -Dipropylamino- and $\alpha\beta$ -Dialkylamino-propionic Acids.*

By EDWARD PERCY FRANKLAND and HENRY EDGAR SMITH.

In the present paper the authors show that propylamine and alkylamine react with  $\alpha\beta$  dibromopropionic acid to form dialkylamino-acids (I) analogous in structure to the dimethylaminopropionic acid obtained by Tafel and E. P. Frankland (*Ber.*, 1909, **42**, 3138) from deoxycaffeine, and yielding nitroso- and carbamido-derivatives analogous to those obtained by E. P. Frankland (*T.*, 1910, **97**, 1686) from dibenzylaminopropionic acid; thus, from dipropylaminopropionic acid it was found possible to synthesise a substance having the composition of 1:7-dipropyltetrahydrouic acid (V).

The two alkylamino-acids are strong bases, uniting with an equivalent of hydrobromic acid when prepared by the action of the amine on dibromopropionic acid in alcoholic solution. An attempt to isolate the free dipropylamino-acid gave rise to a substance which, in its non-crystalline character, resembled the corresponding dimethylamino-acid and diaminopropionic acid itself. Both the new acids yield crystalline salts with hydrobromic and with nitric acids, nitroso-derivatives, presumably of the type indicated in formula (II), carbamido-derivatives (III) by the addition of cyanic acid [reasons for the  $\alpha$ -derivative being formed have been suggested in a previous paper (E. P. Frankland, *loc. cit.*)], hydantoin hydrochlorides (IV) by dehydration with 25 per cent.

hydrochloric acid, and, in the case of the propylamino-compounds, by the further addition of cyanic acid, a substituted tetrahydric acid (V):



## EXPERIMENTAL.

A. Propylamino-derivatives:  $\alpha\beta$ -Dipropylaminopropionic Acid Hydrobromide.

Fifty grams of dibromopropionic acid dissolved in 350 c.c. of absolute ethyl alcohol were treated with 63.5 grams of propylamine (5 molecules), and the mixture heated to boiling under reflux for one and a-half hours. The solution, which became warm on adding the amine, and developed a yellow colour, darkened considerably on heating. The alcohol and the excess of propylamine were then removed by distillation, and the residue was treated with an excess of aqueous baryta in order to decompose the propylamine hydrobromide formed during the reaction. The liberated propylamine was distilled off under diminished pressure, the solution freed from barium by the addition of the requisite amount of sulphuric acid, and the barium sulphate removed. The filtrate, which contained neither barium nor sulphuric acid, was evaporated to a small bulk on the steam-bath, and finally concentrated to a brown, pasty mass in a vacuum desiccator. On treatment with a small quantity of pyridine, the dipropylaminopropionic acid hydrobromide could be separated as a white solid, the impurities being removed by the pyridine. The substance was crystallised from aqueous ethyl alcohol, from which it was deposited in minute needles melting and decomposing at  $200^\circ$ .\* It was very readily soluble in cold water, the solution being neutral to litmus, sparingly soluble in hot alcohol, and insoluble in ether. The yield of this substance was 60 per cent. of that required by theory:

$\text{H}1265$  gave 90.36 c.c.  $\text{CO}_2$  and 9.86 c.c.  $\text{N}_2$ .† C = 40.37; N = 10.28.

$\text{H}1090$  „ 0.0762 AgBr. Br = 29.75.

$\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2 \cdot \text{HBr}$  requires C = 40.15; N = 10.11; Br = 29.74 per cent.

\* All temperatures here given are uncorrected.

† Carbon and nitrogen combustion in a vacuum. Dry  $\text{CO}_2$  and  $\text{N}_2$  at N.T.P.

Smaller yields of the same substance were obtained from solutions of dibromopropionic acid in benzene and in chloroform.

*Dipropylaminopropionic Acid Nitrate.*

A small quantity of dipropylaminopropionic acid hydrobromide was dissolved in water and treated with a solution of silver nitrate (slight excess over 1 molecule). The mixture was heated on the steam-bath for about an hour, the silver bromide separated, and the slight excess of silver in solution precipitated with hydrogen sulphide. The solution, which had thus been freed from silver, was concentrated and stirred with alcohol, whereupon the nitrate of dipropylaminopropionic acid separated in minute needles, melting and decomposing at 170°. The properties of this substance agreed with those of the hydrobromide:

0.0508 gave 6.77 c.c.  $N_2$ .  $N = 16.76$ .

$C_9H_{20}O_2N_2.HNO_3$  requires  $N = 16.73$  per cent.

*Mononitrosodipropylaminopropionic Acid.*

Fifteen grams of dipropylaminopropionic acid hydrobromide were dissolved in a small quantity of water, and treated with silver nitrite (slight excess over one molecule), the mixture being kept cool with ice for about three hours. The silver bromide was then separated, and the excess of silver in solution precipitated by the addition of a drop of dilute hydrochloric acid. The solution, which had been freed from silver, was concentrated in a vacuum desiccator, whereupon the nitroso-compound was deposited in stellate groups of thin prisms. The substance darkened above 200°, and melted with vigorous decomposition at 227°; it was only sparingly soluble in hot water or hot alcohol, and insoluble in ether, the aqueous solution being neutral to litmus. The yield was theoretical. The presence of a nitroso group was confirmed by the Liebermann test:

0.1101 gave 101.6 c.c.  $CO_2$  and 17.1 c.c.  $N_2$ .  $C = 49.68$ ;  $N = 19.52$ .

$C_9H_{19}O_3N_2$  requires  $C = 49.77$ ;  $N = 19.36$  per cent.

*$\beta$ -Propylamino- $\alpha$ -propylcarbamidopropionic Acid.*

A concentrated aqueous solution of 10 grams of dipropylaminopropionic acid hydrobromide was treated with potassium cyanate (slight excess over two molecules), followed by dilute hydrochloric acid (one molecule), and the mixture allowed to remain overnight. On evaporating to a small bulk in a vacuum desiccator, long, needle-shaped crystals were deposited. These were collected, washed with alcohol and with ether, and dried. The product was separated by

treatment with hot alcohol into a sparingly soluble fraction, melting and decomposing at  $216-217^{\circ}$ , and a more readily soluble fraction melting and decomposing at  $210^{\circ}$ . Both fractions crystallised in prisms. The results of analyses showed the more soluble substance to be the monocarbamido-derivative. It was readily soluble in water, only sparingly so in hot alcohol, and insoluble in ether:

0.1663 g. gave 0.3141  $\text{CO}_2$  and 0.1314  $\text{H}_2\text{O}$ .  $\text{C}=51.51$ ;  $\text{H}=8.78$ .  
 0.1009 " 96.66 c.c.  $\text{CO}_2$  and 14.66 c.c.  $\text{N}_2$ .  $\text{C}=51.58$ ;  $\text{N}=18.25$ .  
 $\text{C}_{10}\text{H}_{21}\text{O}_3\text{N}_3$  requires  $\text{C}=51.95$ ;  $\text{H}=9.09$ ;  $\text{N}=18.18$  per cent.

The less soluble substance, which crystallised out first from the mother liquor, gave the following figures on analysis:

0.1004 gave 83.89 c.c.  $\text{CO}_2$  and 18.87 c.c.  $\text{N}_2$ .  $\text{C}=44.98$ ;  $\text{N}=23.61$ .  
 0.1014 " 84.49 c.c.  $\text{CO}_2$  " 19.03 c.c.  $\text{N}_2$ .  $\text{C}=44.86$ ;  $\text{N}=23.58$ .

The average ratio of nitrogen to carbon is thus 1:2.22, instead of 1:3.33, as required by the substance having the formula  $\text{C}_{10}\text{H}_{21}\text{O}_3\text{N}_3$ .

*$\gamma$ -Propylaminomethyl- $\beta$ -propylhydantoin Hydrochloride.*

2.4 Grams of the crude carbamido-derivative described above were dissolved in a small quantity of 25 per cent. hydrochloric acid, and heated on the steam-bath until a white, crystalline product was deposited. This was collected and recrystallised from aqueous alcohol. The substance forms long prisms (from alcohol), melting and decomposing at  $247^{\circ}$ ; very readily soluble in water, with a strongly acid reaction to litmus, sparingly soluble in alcohol, and insoluble in ether. Yield, 88.5 per cent. of that required by theory:

0.0876 gave 78.22 c.c.  $\text{CO}_2$  and 11.86 c.c.  $\text{N}_2$ .  $\text{C}=48.07$ ;  $\text{N}=17.00$ .  
 0.2247 " 0.1290  $\text{AgCl}$ .  $\text{Cl}=14.20$ .  
 $\text{C}_{10}\text{H}_{20}\text{O}_3\text{N}_3\text{HCl}$  requires  $\text{C}=48.29$ ;  $\text{N}=16.90$ ;  $\text{Cl}=14.29$  per cent.

*1:7-Dipropyltetrahydrouic Acid.*

A small quantity of the hydantoin hydrochloride was dissolved in water and treated with a concentrated aqueous solution of potassium cyanate (slight excess over 1 molecule). After remaining at room temperature for three hours the mixture was evaporated to dryness on the steam-bath, and the oily residue extracted with hot alcohol. The tetrahydrouic acid crystallised from the alcoholic solution in minute needles, a theoretical yield being obtained. After recrystallisation from alcohol it melted and decomposed at  $184.5^{\circ}$ . It was soluble in water or hot alcohol, and insoluble in ether; the aqueous solution being neutral to litmus:

0.0922 gave 87.65 c.c.  $\text{CO}_2$  and 16.08 c.c.  $\text{N}_2$ .  $\text{C}=51.18$ ;  $\text{N}=21.91$ .  
 $\text{C}_{11}\text{H}_{20}\text{O}_3\text{N}_4$  requires  $\text{C}=51.56$ ;  $\text{N}=21.88$  per cent.



*B. Allylamino-derivatives: αβ-Diallylaminopropionic Acid Hydrobromide.*

This substance was prepared in the same manner as the corresponding propylamino-compound; 50 grams of dibromopropionic acid in 350 c.c. absolute ethyl alcohol with allylamine in the proportion of four and a-half molecules to one of the acid, giving a 51 per cent. yield of the required amino-acid hydrobromide.

The substance crystallised from aqueous alcohol in minute needles melting and decomposing at 182°. It was very readily soluble in water, sparingly so in alcohol, and insoluble in ether:

0.1250 gave 94.95 c.c. CO<sub>2</sub> and 10.55 c.c. N<sub>2</sub>. C=40.89; N=10.60.

0.1034 „ 0.0733 AgBr. Br=30.17.

C<sub>9</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>.HBr requires C=40.76; N=10.57; Br=30.18 per cent.

*Diallylaminopropionic Acid Nitrate.*

Prepared as in the case of the corresponding propylamino-compound and having similar properties. Minute needles (from aqueous alcohol), melting and decomposing at 165°:

0.0542 gave 7.33 c.c. N<sub>2</sub>. N=16.99.

C<sub>9</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>.HNO<sub>3</sub> requires N=17.00 per cent.

*Mononitrosodiallylaminopropionic Acid.*

This was prepared as in the case of the corresponding propylamino-compound, and had similar properties. It forms colourless, rectangular plates (from water), darkening above 180°, and melting with vigorous decomposition at 204°:

0.0942 gave 88.22 c.c. CO<sub>2</sub> and 14.84 c.c. N<sub>2</sub>. C=50.42; N=19.73.

C<sub>9</sub>H<sub>13</sub>O<sub>3</sub>N<sub>3</sub> requires C=50.70; N=19.77 per cent.

*Action of Bromine on Diallylaminopropionic Acid Hydrobromide.*

A dilute aqueous solution of the hydrobromide was cooled in a freezing mixture and treated drop by drop with bromine (four molecules), the mixture being frequently stirred.

A pasty, orange-coloured substance was deposited, which, after being thoroughly stirred with the mother liquor, was collected, dissolved in alcohol, and reprecipitated with ether as a pale yellow, flocculent compound, darkening and smelling of bromine on keeping in a vacuum desiccator. On heating, it swelled up between 70°

and 50%; at 100° the yellow colour had disappeared, and a colourless glass remained, which decomposed between 130° and 135°. After further purification by means of alcohol and ether and keeping in a vacuum desiccator, the yellow colour disappeared and an amorphous powder remained, insoluble in cold water and in ether, soluble in warm alcohol:

0.1164 gave 0.1630 AgBr. Br=59.59.

$C_8H_{16}O_2N_2Br_4$ \* requires Br=63.49 per cent.

*β-Allylamino-α-allylcarbamidopropionic Acid.*

This substance was prepared under the same conditions as those described for the corresponding propylamino-compound. 12.5 Grams of diallylamino-propionic acid hydrobromide yielded 5.0 grams of a white product, separating in aggregates of minute, needle-shaped crystals. It was collected, washed with alcohol and with ether, and, after drying, melted and decomposed at 194°. After four recrystallizations from aqueous alcohol the melting point was raised to 204.5°. The substance was very readily soluble in water, sparingly so in alcohol, and insoluble in ether:

0.0902 gave 87.85 c.c. CO<sub>2</sub> and 13.43 c.c. N<sub>2</sub>. C=52.43; N=18.70.

$C_{10}H_{17}O_3N_3$  requires C=52.86; N=18.50 per cent.

*γ-Allylamino-methyl-β-allylhydantoin Hydrochloride.*

1.2 Grams of the substance described above were converted by the action of 25 per cent. hydrochloric acid into the hydantoin compound, as described in the case of the propylamino-derivative. A theoretical yield was obtained. The substance separated from aqueous alcohol in long prisms, melting and decomposing at 217°. It is extremely soluble in water, sparingly so in alcohol, and insoluble in ether. The aqueous solution was strongly acid to litmus:

0.0932 gave 84.86 c.c. CO<sub>2</sub> and 12.81 c.c. N<sub>2</sub>. C=49.02; N=17.27.

0.1990 " 0.1165 AgCl. Cl=14.49.

$C_{12}H_{15}O_2N_3.HCl$  requires C=49.08; N=17.18; Cl=14.52 per cent.

1.3 Grams of the hydantoin hydrochloride were treated with potassium cyanate (slight excess over 1 molecule) in aqueous solution. On evaporating to dryness and extracting the residue with alcohol, a colourless, oily product was obtained. This was collected and dried in a vacuum desiccator, and, on grinding, appeared as a hygroscopic, amorphous powder. Yield, 1.5 grams. This

\* Tetrabromodipropylaminopropionic acid.

substance did not appear to be the required allyltetrahydronic acid, or, at all events, only an impure specimen of it, analysis showing both the nitrogen and the carbon to be several per cent. lower than the proportions required by theory.

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### CVI.—*The Estimation of Zinc as Zinc Ammonium Phosphate and Zinc Pyrophosphate.*

By THOMAS MATTHEW FINLAY and ALEXANDER CHARLES CUMMING.

THE method of estimating zinc as zinc ammonium phosphate was first recommended by Tamm (*Chem. News*, 1871, **24**, 148), and has since been investigated by Clark (*J. Soc. Chem. Ind.*, 1896, **15**, 866), Gooch and Austin (*Amer. J. Sci.*, 1898, **6**, 223), and notably by Dakin (*Zeitsch. anal. Chem.*, 1901, **39**, 273).

As Dakin's procedure was closely followed in the experiments of which the results are given in table III, and was found to yield very satisfactory results when a pure zinc solution was used, a brief description may be given.

*Dakin's Method.*—The acid zinc solution, contained in a platinum basin, is almost, but not quite, neutralised with ammonia, diluted to 150 c.c., and warmed on the water-bath. To the warm solution ammonium phosphate is added, the weight of the ammonium phosphate being about ten times the probable weight of the zinc. The precipitate, which is amorphous at first, quickly changes to a fine crystalline precipitate of zinc ammonium phosphate,  $\text{ZnNH}_4\text{PO}_4$ . This change takes place more quickly in presence of a considerable amount of ammonium salts.

The solution is heated for fifteen minutes on the water-bath, and set aside for some time. The precipitate is filtered through a Gooch crucible, washed with 1 per cent. ammonium phosphate until free from chloride, and then several times with alcohol or cold water. It is dried at 100–105°, and weighed as  $\text{ZnNH}_4\text{PO}_4$ , or, after ignition with exclusion of flame gases, as  $\text{Zn}_3\text{P}_2\text{O}_7$ .

Dakin also states that where large amounts of ammonium salts are present, it is preferable to ignite directly to the pyrophosphate, owing to the difficulty of removing these salts completely by washing.

Low ("Technical Methods of Ore Analysis," 1911, p. 301) recom-

mends the use of microcosmic salt as precipitant, and to the solution after neutralisation with ammonia he adds 1 c.c. of acetic acid. In some experiments in this laboratory his method was followed, and as the results were sometimes accurate and sometimes very unsatisfactory, a systematic investigation of the method appeared desirable, as it was evident that some slight variation in the conditions of precipitation was the source of the large error.

*Effect of Acidity on the Character of the Precipitate.*—The error noted above was found to be due to precipitation in a solution which was too acid. The precipitate obtained from a neutral solution or one which contained only a trace of free acetic acid was homogeneous, consisting of pure zinc ammonium phosphate. The precipitate obtained from a solution to which 1 c.c. of glacial acetic acid had been added after neutralisation was found, by microscopic examination, to be a mixture of three substances. One portion was amorphous, and consisted of zinc hydroxide or a basic phosphate; a second portion had the characteristic crystalline form of zinc ammonium phosphate; the third portion consisted of groups of needle-shaped crystals, which tended to arrange themselves in tufts round a common nucleus. These crystals imparted to the precipitate its characteristic flocculent appearance. It appeared probable that these crystals were sodium zinc phosphate, and experiment confirmed this supposition. An almost homogeneous precipitate of zinc sodium phosphate was prepared by addition of sodium phosphate to a pure zinc sulphate solution. The crystals thus obtained showed the crystalline arrangement described above.

Zinc sodium phosphate is readily hydrolysed; even on washing with cold water it becomes transformed into amorphous zinc hydroxide or a basic phosphate.

When zinc is precipitated from an acid solution, some zinc remains in solution, but the error from this source is small in comparison with the total error.

#### EXPERIMENTAL.

In all experiments, the amount of zinc present was known from the weight of pure zinc sulphate taken.

*Precipitation with Microcosmic Salt in Acid Solution.*—Table I shows the large error introduced by precipitation in a too strongly acid solution. In these experiments, the zinc was precipitated with microcosmic salt, the solution neutralised with ammonia, and 1 c.c. of glacial acetic acid added. The precipitate was ignited and weighed. Column IV gives the weight of zinc on the assumption that the residue was pure zinc pyrophosphate.

TABLE I.

No.	Zn taken.	Wt. of ppt.	Zn found.	Error.
1	0.1389	0.2676	0.1148	-0.0241
2	0.1599	0.2892	0.1241	0.0358
3	0.2195	0.4198	0.1801	0.0394

The large error is due to the false assumption that the residue was zinc pyrophosphate. Since zinc sodium phosphate forms part of the precipitate, one would expect high results. The results in practice are low, since zinc sodium phosphate is largely hydrolysed by the wash-water, the final residue being largely zinc hydroxide, or a basic salt.

*Precipitation with Microcosmic Salt in Slightly Acid Solution.*—

To prevent precipitation of the hydroxide, it is necessary to keep the solution on the acid side of neutrality. Table II gives the results obtained by precipitation with microcosmic salt. After addition of the microcosmic salt, the solution was neutralised with ammonia and then made faintly acid with acetic acid. The precipitate was ignited and weighed as pyrophosphate.

TABLE II.

No.	Zn taken.	$\text{Zn}_2\text{P}_2\text{O}_7$ .	Zn found.	Error.
1	0.1993	0.1658	1.1999	+0.0006
2	0.1909	0.1462	0.1915	0.0006
3	0.2229	0.5218	0.2239	0.0010

It is evident that accurate results are obtainable by precipitation with microcosmic salt, but, as there is less liability to error, we regard precipitation with ammonium phosphate as preferable.

*Precipitation with Ammonium Phosphate.*—Table III shows the results obtained by Dakin's method, that is, precipitation with ammonium phosphate in neutral or faintly acid solution. The first half of the table gives the zinc estimated as  $\text{ZnNH}_4\text{PO}_4$ , the second half as  $\text{Zn}_2\text{P}_2\text{O}_7$ . In No. 5 a platinum vessel was used, and the precipitate showed a tendency to adhere to the sides of the vessel, a difficulty which was not experienced with glass vessels unless a large quantity of ammonium salt was present.

TABLE III.

No.	Zn taken.	$\text{ZnNH}_4\text{PO}_4$ found.	Zn found.	Error.
1	0.1722	0.1708	0.1726	+0.0001
2	0.2015	0.5516	0.2022	+0.0007
3	0.1839	0.5038	0.1846	+0.0007
4	0.2017	0.5520	0.2023	+0.0006
5	0.1536	0.4452	0.1632	-0.0004
6	0.1588	0.4336	0.1590	+0.0002
7	0.1778	0.4854	0.1779	+0.0001

TABLE III (*continued*).

No.	Zn taken.	Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> found.	Zn found.	Error.
1	0.1722	0.4037	0.1732	+0.0010
2	0.2015	0.4706	0.2019	+0.0004
3	0.1633	0.4298	0.1844	+0.0005
4	0.2017	0.4716	0.2023	+0.0006
5	0.1636	0.3794	0.1628	-0.0008
6	0.1588	0.3716	0.1595	+0.0007
7	0.1778	0.4156	0.1783	+0.0005

These results show that accurate results are obtained with a pure zinc solution if Dakin's procedure is closely followed. Inaccurate results, however, will be obtained (1) if the solution is alkaline, or (2) if the solution contains any free mineral acid or more than a trace of free acetic acid.

As commercial "ammonium phosphate" is not always the same salt, it is preferable to neutralise with ammonia after addition of ammonium phosphate, and then add 1 c.c. of dilute (about 2*N*) acetic acid. With this procedure it is immaterial whether one uses an acid phosphate or the normal phosphate.

*Precipitation with Potassium and Sodium Phosphates.*—The precipitate obtained when potassium or sodium phosphate is added to a zinc salt in neutral solution behaves like zinc ammonium phosphate, being amorphous at first, but crystallising on keeping. The peculiar crystalline appearance of zinc sodium phosphate has already been noticed; the potassium compound is rather finer-grained than zinc ammonium phosphate. Both zinc potassium phosphate and zinc sodium phosphate remain unchanged on further heating after their water of crystallisation has been driven off. Experiments were carried out to see whether these salts would be suitable forms in which to estimate zinc. The results with potassium proved nearly quantitative, those with sodium were very low. The zinc was completely precipitated in both cases, and the error was apparently due to the fact that both salts are hydrolysed by the subsequent washing water, for phosphate could always be detected in the filtrate even after prolonged washing, although no zinc was dissolved. In the case of zinc potassium phosphate, the loss due to hydrolysis was slight, but increased the more thorough the washing. This will be seen from the following table, where Nos. 1 and 2 show the results after washing about six to eight times, Nos. 3 and 4 show the effect of longer washing, and Nos. 5 and 6 the effect of very prolonged washing. The final washings in all cases contained phosphate, but no zinc. Zinc potassium phosphate is therefore not a suitable form in which to estimate zinc.

TABLE IV.

*Precipitation with Potassium Phosphate in Neutral Solution.*

No.	Zn taken.	ZnKPO <sub>4</sub> found.	Zn found.	Error.
1	0.1775	0.5392	0.1767	-0.0008
2	0.1629	0.5124	0.1630	0.0001
3	0.1909	0.5774	0.1893	0.0016
4	0.1555	0.4691	0.1539	0.0016
5	0.1789	0.5364	0.1758	0.0032
6	0.1659	0.4998	0.1639	0.0020

*Precipitation with Ammonium Phosphate in Presence of Sodium and Potassium Salts.*

Whilst the sodium and potassium compounds are not suitable forms in which to estimate zinc, the fact of their formation must be taken into account when precipitating in presence of sodium and potassium salts, for, as might be expected, a mixture of zinc ammonium phosphate and zinc potassium phosphate or zinc sodium phosphate is precipitated. Sodium salts do not present much difficulty, as they can be completely removed in a single precipitation, provided the solution is not too acid and a sufficient quantity of ammonium salt is added. Even when large quantities of sodium salts are present, they can be removed in this way. For example, 5.0 grams of sodium chloride were added to a zinc solution. The zinc was precipitated by ammonium phosphate after addition of 10 grams of ammonium chloride. The precipitate was ignited and weighed as pyrophosphate. Zn taken=0.1965; Zn found=0.1963.

Potassium salts are not removed so easily. A single precipitation, even in presence of a large quantity of ammonium salts, is insufficient to prevent partial precipitation of the potassium salt; a double precipitation is necessary, and a large amount of ammonium chloride must be added before each precipitation. A reference to table VI will show that, for complete removal of potassium, it was necessary to add 10 grams of ammonium chloride before each precipitation.

When such large quantities of ammonium salts were present, the precipitate was found to adhere strongly to the sides of the glass beakers used, and could not be completely removed by rubbing. In such cases the traces were dissolved in a little hydrochloric acid and reprecipitated. Dakin has pointed out that when zinc ammonium phosphate is precipitated in presence of large amounts of ammonium salts, it is impossible to remove all the ammonium salts by washing; in all such cases, the precipitate was therefore ignited and weighed as pyrophosphate.

Table V gives the results of estimations in presence of potassium salts. Nos. 1, 2, and 3 were precipitated once. With Nos. 4 and 5 the given amount of ammonium chloride was added before precipitation with ammonium phosphate. The precipitate was collected, washed two or three times, and redissolved in a small quantity of hydrochloric acid. This solution was then neutralised, and the zinc precipitated as before, but without addition of ammonium chloride.

TABLE V.

No.	Zn taken.	KCl added.	NH <sub>4</sub> Cl added.	Zn found.	Error.
1	0.1726	1.0	none	0.1901	+0.0175
2	0.1844	2.0	"	0.2036	+0.0192
3	0.1772	3.0	10 grams	0.1920	+0.0148
4	0.1576	3.0	10 "	0.1640	+0.0064
5	0.1882	3.0	10 "	0.1950	+0.0068

These results indicate that the amount of potassium in the precipitate may be reduced (1) by a double precipitation, and (2) by adding a large quantity of ammonium chloride before precipitation. Some experiments were therefore tried on the effect of a double precipitation with addition of ammonium chloride before each precipitation. The results are given in table VI. The fourth column gives the amount of ammonium chloride added before both the first and second precipitation.

TABLE VI.

No.	Zn taken.	KCl added.	NH <sub>4</sub> Cl added.	Zn found.	Error.
1	0.1778	0.5	5.0	0.1775	-0.0003
2	0.1735	1.0	5.0	0.1745	+0.0010
3	0.1724	1.0	10.0	0.1722	-0.0002
4	0.1418	1.5	10.0	0.1415	-0.0003
5	0.1556	2.0	10.0	0.1559	+0.0003
6	0.1475	3.0	10.0	0.1472	-0.0003

Accurate results are therefore obtainable in presence of potassium by means of a double precipitation with addition of 5 to 10 grams of ammonium chloride before each precipitation.

*Composition of Precipitated Zinc Ammonium Phosphate and Zinc Potassium Phosphate.*—According to Tamm and Dakin, the composition of the precipitated ammonium salt is anhydrous  $\text{ZnNH}_4\text{PO}_4$ , but Low gives it as  $\text{ZnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ . Experiments on the salt, dried in the air for an hour on a porous plate, showed that constant weight was obtained at  $110^\circ$ , the salt having lost only 0.15 per cent. of its weight; it is therefore anhydrous zinc ammonium phosphate, since the monohydrate would lose 9.2 per cent. by weight on drying. At  $150^\circ$  the salt begins to decompose, leaving



the pyrophosphate. Ammonia is freely evolved as the temperature reaches  $200^{\circ}$ . A sample of precipitated zinc potassium phosphate was dried in the air and weighed. On heating, it became anhydrous at  $105^{\circ}$ , the loss of weight corresponding with four molecules of water. Precipitated zinc potassium phosphate is therefore probably  $\text{ZnKPO}_4 \cdot 4\text{H}_2\text{O}$ , but owing to the difficulty of preparing it in a state of purity this result cannot be considered conclusive.

#### Summary.

The phosphate method for the estimation of zinc has been investigated to find the reason for occasional unsatisfactory results. It was found that salts of the composition  $\text{ZnNaPO}_4$  and  $\text{ZnKPO}_4$  are formed if the solution contains sodium or potassium salts. Precipitation with microcosmic salt yields inaccurate results unless special care is taken to neutralise the solution or to render it very slightly acid with acetic acid after precipitation. In the presence of sodium salts, correct results are obtained by precipitation with ammonium phosphate in neutral solution, after addition of 5 to 10 grams of ammonium chloride. If potassium is present, ammonium chloride must be added before precipitation of the zinc with ammonium phosphate, the precipitate re-dissolved, more ammonium chloride added, and the zinc reprecipitated as before. The precipitate must be ignited and weighed as pyrophosphate.

If due attention is paid to these points, one obtains a crystalline precipitate which is easily manipulated. For a pure zinc solution no more satisfactory method could be desired; in presence of sodium or potassium (more particularly the latter), the method is less satisfactory, but yields accurate results.

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### CVII.—*Mechanism of the Transformation of Ammonium Cyanate into Carbamide, and of the Decomposition of Carbamide by Heat. The Polymerisation of Cyanic Acid.*

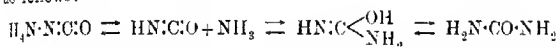
By EMIL ALPHONSE WERNER.

THE interesting researches of Walker and his co-workers (T., 1895, 67, 746; 1897, 71, 489) have supplied us with most of our present knowledge regarding the phenomena which accompany the trans-

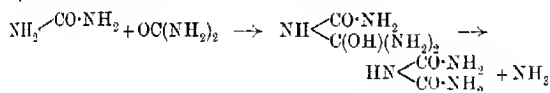
formation of ammonium cyanate into carbamide, both in the dry state and in aqueous or alcoholic solution.

The following are perhaps the most important established facts which support the views and experimental results that form the subject of the present communication: (1) The bimolecular order of the change. (2) The reversibility of the transformation. (3) The partial hydrolysis of ammonium cyanate with production of ammonium carbonate which accompanies the transformation; and (4) The greatly increased velocity of the change of ammonium cyanate into carbamide in an alcoholic, as compared with an aqueous, solution.

Quite recently Chattaway (T., 1912, 101, 170) has put forward a theory by the aid of which he proposes to explain, not only the probable changes which occur during the transformation of ammonium cyanate into carbamide, but also to account for the formation of biuret and cyanuric acid by the further action of heat on the amide. These changes, together with several related reactions in which cyanic acid and its esters are concerned, he considers may all be simply explained by the well known tendency of the carbonyl group to add on other groups, such as  $\text{R}_2\text{N} > \text{NH}$  or  $\text{R} \cdot \text{OH}$ , followed by a subsequent rearrangement involving the migration of a hydrogen atom from oxygen to nitrogen; thus the primary change of ammonium cyanate into carbamide is formulated as follows:



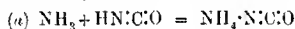
whilst the production of biuret is explained in accordance with the equation:



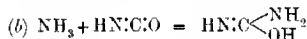
the amino-group of one molecule of carbamide reacting with the carbonyl group of another, the hypothetical intermediate product giving rise to biuret by loss of ammonia, and by a repetition of these changes, cyanuric acid is ultimately formed, no less than three hypothetical intermediate products being supposed to take part in the changes before the atomic complex,  $\text{HN} < \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > \text{CO}$ , is produced. Whilst this can scarcely be considered a simple explanation of the phenomena in question, this theory, as is pointed out in the following, is open to several serious objections, besides which it fails to explain some of the established facts connected with the

different changes, and in the present author's opinion does not possess the required agreement with experimental evidence to secure its general acceptance as a likely explanation of the well known reactions under consideration.

Commencing with the primary change, the first point subject to criticism is the constitution of ammonium cyanate itself. Chattaway considers this salt to be derived from the *iso*-, or, more correctly, the keto-form of the acid; and as dissociation proceeds with application of heat, the dissociated products re-unite to form carbamide, no change in the constitution of the cyanic acid being assumed to occur. Bearing in mind that the many reactions, attributed to the tendency of the carbonyl group to add on such groups as cited by Chattaway, take place readily at the ordinary temperature, it is difficult to understand why ammonium cyanate should be produced at all if cyanic acid is considered to be  $\text{H}\cdot\text{N}:\text{C}:\text{O}$  only; for instance, there seems no reason why the two reactions:



and



should take place at the same temperature (see Expts. 1, 2, 3, and 4), unless it be assumed that cyanic acid at low temperatures is predisposed to react in accordance with equation (a), since at 0°, for example, the product of the interaction is ammonium cyanate only. That a condition of equilibrium between the reaction products should be capable of arising from such a cause is very improbable.

If a change in the configurations of the cyanic acid molecule from  $\text{HO}\cdot\text{C}:\text{N}$  to  $\text{HN}:\text{C}:\text{O}$  with rise of temperature be admitted, all the phenomena connected with the transformation of ammonium cyanate into carbamide and of the decomposition of the latter by heat can be easily explained in a very simple manner, which is, moreover, shown in the following to be in complete accord with all the known facts.

It is only necessary to refer in general to the extensive work of E. Fisher on uric acid and its derivatives, and in particular to the interesting results of Hantzsch and Bauer (*Ber.*, 1905, **38**, 1005) and Hantzsch (*Ber.*, 1906, **39**, 139) on the constitution of the metallic salts of cyanuric acid and on the production of mixed *N*-alkyl and *O*-alkyl derivatives, to show that the formation of derivatives containing the complex  $\text{R}\cdot\text{O}\cdot\text{C}:\text{N}\cdot$  from compounds containing the group  $\cdot\text{NH}\cdot\text{CO}\cdot$  is determined by the electropositive character of the element or radicle taking part in the change.

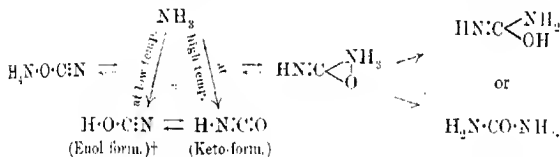
It seems only natural to suppose that the group  $\text{HN}:\text{CO}$ , in the

free state, should behave in a similar manner, under the same influence. The experimental results, in fact, appear to favour the view that cyanic acid is capable of existing in equilibrium in the two forms, the relative proportions being a function of the temperature.

The two best known properties of ammonium cyanate, namely, its hydrolysis to ammonium carbonate, noticed by Walker (*loc. cit.*), and its transformation into carbamide are strong evidence in support of the constitutional formula  $\text{H}_2\text{N}\cdot\text{O}\cdot\text{CN}$ ; thus, cyanic acid in its enolic form may be considered as "carbonitril," and the hydrolysis of the ammonium salt expressed as follows:

$\text{H}_2\text{N}\cdot\text{O}\cdot\text{CN} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{ONH}_4$ , ammonium carbamate being, no doubt, an intermediate product. Assuming the formula  $\text{H}_2\text{N}\cdot\text{N}\cdot\text{C}\cdot\text{O}$ ,\* the change by hydrolysis is by no means simple to follow, even admitting the presence of the ions  $\text{H}_2\text{N}$  and  $\text{NCO}$  in solution.

Being a weak acid in the enolic form (comparable to  $\text{HOCl}$ ), cyanic acid would naturally yield a very unstable ammonium salt, easily dissociated by heat, both in the dry state and in solution, and transformable into carbamide according to the following scheme:



The formula  $\text{HN}\cdot\text{C}\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{O} \end{array}$ , which is used in the above to show the production of carbamide from the union of ammonia with  $\text{H}\cdot\text{N}\cdot\text{C}\cdot\text{O}$ , is an extension of the formula recently proposed by the author to represent the constitution of thiocarbamide in the static condition (J., 1912, 101, 2185): no particular stress is laid on its acceptance in the above scheme until experimental evidence is forthcoming to support it, and whilst it helps to throw some light

\* This constitution is based solely on analogy to  $\text{KCN}$ ; reactions of the type  $\text{KCN} + \text{RX} \rightarrow \text{R}\cdot\text{NCO} + \text{KX}$  are no proof that the potassium salt must be  $\text{KNC}$ : the constitution depends entirely on the electro-chemical nature of the element or radical entering into the change: the properties of potassium cyanate are more in agreement with the constitution  $\text{KOCN}$  than  $\text{KNC}$ .

† Since the group  $\text{HN}\cdot\text{CO}$  shows great analogy in its behaviour to the group  $\text{CH}_2\cdot\text{CO}$ , the distinctive terms "enol" and "keto" are equally well applicable to the former group, and are used here in preference to the usual unsuitable terms "a-enol" and "iso" for the two forms of cyanic acid.

on the ultimate appearance of carbamide in either the symmetrical or unsymmetrical form, it is obvious that its removal from the scheme will not affect the meaning which this is intended to convey. Whilst carbamide is much more stable than ammonium cyanate, when it is heated above its melting point it also undergoes dissociation into ammonia and cyanic acid (chiefly in the keto-form), and gives a sublimate which, under ordinary conditions contains from 28 to 30 per cent. of ammonium cyanate, whilst if the vapours are artificially cooled, this may be increased to over 40 per cent. (see Experimental part); the rest of the sublimate is carbamide; if the vapour is kept warm, the sublimate, as might be expected, consists entirely of carbamide.

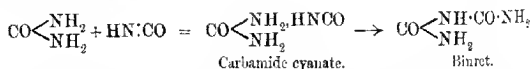
These results show that the dissociation product must contain cyanic acid both in the enol and keto-forms, the proportions varying with the temperature; the enol form, which is alone responsible for the presence of ammonium cyanate in the sublimate, is not capable of existing at the higher temperature.

The reversion of carbamide to ammonium cyanate first pointed out by Walker and Hambley (*loc. cit.*) is easily explained by the views embodied in the above scheme; it is evident that carbamide undergoes a certain amount of dissociation in aqueous solution, even at the ordinary temperature; under such conditions some of the cyanic acid will assume the enol form, and in presence of ammonia will give rise to the cyanate.

#### *Production of Biuret and Cyanuric Acid from Carbamide.*

The dissociation of carbamide by heat has not been considered by Chittaway in his explanation of the origin of biuret and cyanuric acid respectively by the decomposition of the amide, stress being laid solely on the evolution of ammonia, and both products are supposed to be formed by the mutual interaction of carbamide molecules in the manner already referred to.

All the experimental evidence, however, is in favour of the view that the cyanic acid set free by dissociation is responsible for the production of the biuret and cyanuric acid, the former resulting from its reaction with unchanged carbamide in the following manner:



As is well known, when carbamide is heated alone the yield of biuret is very poor; the conditions are unfavourable for the realisation of the above reaction, much of the cyanic acid undergoes

polymerisation to cyanuric acid at the high temperature, whilst another portion is volatilised along with ammonia.

Schiff's improved method for preparing biuret (*Ber.*, 1896, **29**, 298) by heating carbamide hydrochloride to a temperature not exceeding  $130^{\circ}$ , whereby a yield amounting to 45–50 per cent. of the carbamide taken may be easily obtained, is readily explained; the disturbing influence of the ammonia is removed by its conversion into ammonium chloride, whilst the low temperature retards the polymerisation of the cyanic acid.

The above reaction has, in fact, been realised long ago by Finckh (*Annalen*, 1861, **124**, 336), who showed that biuret may be prepared by passing the vapour of cyanic acid directly into carbamide heated to its melting point; moreover, in recent years several substituted biurets and thiobiurets have been prepared by analogous reactions.

When biuret is heated above its melting point ( $190^{\circ}$ ) it decomposes rapidly, giving off ammonia and cyanic acid; by artificially cooling the vapour a quantity of sublimate may be easily obtained; this was found in a single experiment to contain as much as 42–43 per cent. of ammonium cyanate, together with carbamide; the residue after heating was mainly cyanuric acid.

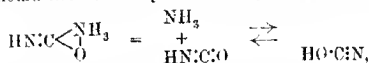
It is evident, therefore, that cyanic acid, as well as ammonia, is produced throughout the whole course of the changes, and since cyanuric acid, as pointed out by Hantzsch (*Ber.*, 1905, **38**, 1013), is a product of the polymerisation of cyanic acid at high temperatures, in contrast to cyamelide which is a product of an analogous change at low temperatures, it seems quite unnecessary to look outside this cause for the origin of cyanuric acid as a product of the decomposition of carbamide. It also explains why the polymeride appears at the very outset of the decomposition of carbamide, simultaneously with the biuret, and if any cyanuric acid is produced other than by polymerisation of  $\text{HN}:\text{C}:\text{O}$ , it seems more likely to result from an interaction between biuret and cyanic acid on the same lines as in the last equation, rather than between biuret and unchanged carbamide, as suggested by Chattaway in his theory.

#### *Constitution of Carbamide in the Static Condition.*

It is rather remarkable that the dissociation of carbamide by heat, with formation of cyanic acid as a volatile product, has not received proper consideration; the general impression appears to be that carbon dioxide is one of the products which accompanies ammonia during the decomposition of carbamide by heat; even in such a recent work as "Organic Chemistry of Nitrogen" (Sidgwick, 1910, p. 186) the following statement occurs: "When urea is

strongly heated it breaks up with the formation of ammonia, carbon dioxide, biuret, and cyanuric acid," the latter being correctly attributed to the rapid polymerisation of cyanic acid as fast as it is set free. It is obvious that the formation of carbon dioxide would involve a secondary decomposition either between two molecules of carbamide, or one in which water is formed, which would then hydrolyse the cyanic acid with production of carbon dioxide.

When the structural formula for carbamide suggested by the writer is considered, there appears no reason why the decomposition by heat should not be a simple and straightforward change, thus.

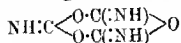


in which no secondary products are formed, so far as the volatile substances are concerned. This view has been confirmed by direct experiment, the results of which prove conclusively that carbon dioxide is not a product of the decomposition by heat of pure dry carbamide. The change is a simple case of dissociation, and, as indicated by the above equation, ammonia and cyanic acid are the sole volatile products, the presence of the latter being, no doubt, responsible for the erroneous idea that carbon dioxide is one of the decomposition products.

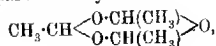
Experimental evidence in support of the constitution of carbamide here proposed is deferred to a future communication.

#### *The Formation of Cyamelide and Cyanuric Acid from Cyanic Acid*

The polymerisation of cyanic acid at low temperatures, with production of cyamelide, has an important bearing on the views put forward by the writer regarding the relations of the two forms of cyanic acid. Van't Hoff ("Chemical Dynamics," p. 110) has shown that the change of cyanic acid to cyamelide is no doubt a ternolecular reaction; Hantzsch (*Ber.*, 1905, **38**, 1016), from a study of its chemical properties, has proposed a constitutional formula for cyamelide which is in all probability a correct representation of the structure of the compound. It is concluded that cyamelide cannot contain either the group HO:CN or the group HN:C:O, and is hence very likely a polymeride resulting from the union of three molecules of cyanic acid through the intervention of oxygen, thus.



and comparable to paracetaldehyde:

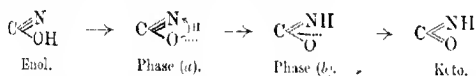


Hantzsch's conclusion that cyamelide must be considered as a condensation product derived from  $\psi$ -cyanic acid, that is, the keto-form,  $\text{HN}(\text{C}\equiv\text{O})$ , does not necessarily follow from the above formula, and is open to criticism, since it still leaves unanswered the question: - Why is cyamelide formed along with cyanuric acid under the conditions stated."

When cyanic acid undergoes polymerisation, the change, as well known, is very rapid, and is accompanied by much development of heat, and the product is a mixture of the two polymerides; in the particular experiment recorded by Senier and Walsh (T., 1902, 81, 290), as much as 70 per cent. of the product was found to be cyanuric acid. Hantzsch's experiments (*loc. cit.*) have shown that the conditions favourable to the formation of cyamelide are slow polymerisation and a low temperature; and Walker's observation of the production of some cyamelide during the slow transformation of ammonium cyanate into carbamide at  $61^{\circ}$  is of particular interest in this connexion.

The mechanism of the formation of cyamelide and cyanuric acid becomes intelligible if the tendency of the two forms of cyanic acid to co-exist in equilibrium be taken into consideration, and may be explained as follows. Cyanic acid represents an unstable group of atoms, which is incapable of assuming a simple \* molecular configuration which can give rise to a condition of static equilibrium, an end which is only attained by polymerisation to a six-membered ring, the most stable form of cyclic molecules.

The enol-form of the acid is apparently the less stable, and tends to change to the more stable keto-form, thus:

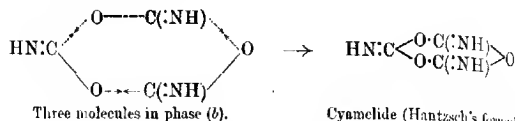


Since an interval of time must elapse, while the hydrogen atom has migrated from oxygen to nitrogen, either a valency of the oxygen atom becomes momentarily free (a), followed immediately by a momentary liberation of a carbon valency (b) when the hydrogen atom unites with nitrogen, or when the hydrogen atom has attained a position as represented in (a) a simultaneous liberation of the respective valencies occurs, their union within the molecule giving rise to the keto-form of the acid. Since this is also an unstable configuration, it is natural to conclude that the chief result will be the formation of cyamelide by the union of three molecules when in the state represented by phase (b), the free valency of the oxygen

\* Neither fulminic acid,  $\text{C}\equiv\text{NOH}$ , nor formonitrile oxide,  $\text{CH}\equiv\text{N}$ , has been isolated.

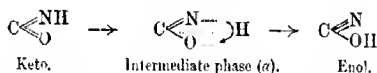


atom of one molecule uniting with the free valency of the carbon atom of another, thus:

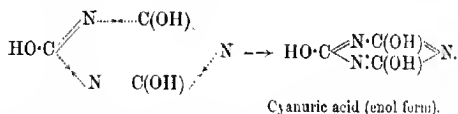


According to this theory, cyanelide is not the result of the polymerisation of cyanic acid pre-existing in the keto-form (*ψ*-acid of Hantzsch), but is the product of the natural tendency to stable equilibrium formed while the acid is in the act of changing from one form to the other. It also explains a third condition which is necessary in order that cyanelide may be formed, namely, that the cyanic acid must be primarily in the enol form.

When cyanic acid is generated at a high temperature, as during the dissociation of carbamide by heat, it is liberated solely in the keto-form, which polymerises at once to cyanuric acid, no cyanelide being formed. In this case the polymerisation originates as follows:



the conditions being altogether unfavourable for the existence\* of  $\text{HO}\cdot\text{C}\cdot\text{N}$ ; the latter cannot be formed by union of the momentary free valencies of the carbon and nitrogen atoms within the molecule itself, and hence a state of stable equilibrium is attained by the union of three molecules in phase (a) to form cyanuric acid the moment the hydrogen atom has entered into union with oxygen, thus:



It is obvious that cyanelide cannot be formed in the above reaction; on the other hand, cyanuric acid is largely formed during the production of cyanelide (Senier and Walsh, *loc. cit.*), a fact which the present theory is capable of predicting, namely, since the keto-form of cyanic acid is produced simultaneously with the cyanelide, in accordance with the first scheme, and also in consequence, simultaneously with the disappearance of the enol acid, it

\* Although  $\text{HO}\cdot\text{C}\cdot\text{N}$  cannot exist free at the temperature, the tendency of  $\text{HN}\cdot\text{C}\cdot\text{O}$  to co-exist in equilibrium with it would still persist, from which cause the polymerisation takes effect.

(the keto acid) becomes immediately polymerised to cyanuric acid in an endeavour to restore equilibrium by giving rise to more of the enol form, in accordance with the second scheme.

There is little doubt that the thermal effect which accompanies the polymerisation of liquid cyanic acid must have an important influence on the relative proportions of the two polymerides produced in a given experiment, and it is very likely that if cyanic acid were allowed to undergo slow polymerisation at a very low temperature a much larger proportion of cyamelide would be produced than was found by Senier and Walsh in the single case recorded by them.

The production of a small quantity of cyamelide from ammonium cyanate at 61° (Walker, *loc. cit.*) confirms the view that cyanic acid in the form  $\text{HO}\cdot\text{C}\equiv\text{N}$  results from the dissociation of the ammonium salt.

The theories which have been put forward in the present communication to explain the several phenomena discussed can lay claim to be in complete agreement with all the experimental facts, and no series of hypothetical intermediate compounds is introduced to hamper their simplicity. All the different changes can be referred to the two fundamental causes:

- (1) Dissociation, and (2) the reversible reaction:



In the face of all the evidence, Chattaway's conclusion that "the oldest and best-known instance of isomeric change is not a case of isomeric change at all" is not justifiable; there exists no reason for removing Wöhler's historical discovery from its time-honoured position of being the first example of isomeric change on record.

#### EXPERIMENTAL.

Qualitative experiments have shown that when carbamide or biuret are decomposed by heating in a long test-tube the sublimate formed consists of ammonium cyanate and carbamide, the proportions of which vary with the temperature and rate of heating.

Soluble cyanates can be rapidly estimated with a fair degree of accuracy by direct titration with  $N/10$ -silver nitrate, using neutral chromate as indicator; the estimation is not interfered with by the presence of carbamide in excess.

Example I: 0.098  $\text{KOCN}$  (Kahlbaum) dissolved in 20 c.c. of water.

$N/10\text{-AgNO}_3$  required = 11.2 c.c.;  $\text{KOCN}$  = 92.5 per cent.

Example II: 0.1935  $\text{KOCN}$  (freshly prepared by action of

potassium hydroxide on urethane in alcoholic solution; Mulder, *Rec. trav. chim.*, 1838, **6**, 170) dissolved in 40 c.c. of water.

$N/10\text{-AgNO}_3$  required = 23.4 c.c.;  $\text{KOCN}$  = 98.07 per cent.

In all the following experiments 4 grams of well-dried powdered carbamide were heated in a dry test-tube 2.5 cm. wide and 18 cm. long, closed with a cork carrying a piece of narrow glass tubing about 15 cm. to exclude moisture from the air during the heating. The tube was held in a nearly horizontal position.

*Expt. 1.*—Carbamide heated at a moderate rate until the liquid just became opalescent. Tube quickly cooled under the water tap, and the greater part of the sublimate removed by means of a steel spatula, and at once analysed.

Sublimate = 0.0241.

$N/10\text{-AgNO}_3$  required = 1.2 c.c.;  $\text{NH}_4\text{OCN}$  = 29.8 per cent.

*Expt. 2.*—Same as above.

Sublimate = 0.09.

$N/10\text{-AgNO}_3$  = 4.4 c.c.;  $\text{NH}_4\text{OCN}$  = 28.8 per cent.

*Expt. 3.*—Carbamide heated slowly, front of tube, to extent of 8 cm., surrounded by a coil of narrow lead piping carrying a current of cold water.

Sublimate = 0.1215.

$N/10\text{-AgNO}_3$  = 7.4 c.c.;  $\text{NH}_4\text{OCN}$  = 36.5 per cent.

*Expt. 4.* Carbamide heated very rapidly, vapour cooled as in *Expt. 3*.

Sublimate = 0.151.

$N/10\text{-AgNO}_3$  = 10.4 c.c.;  $\text{NH}_4\text{OCN}$  = 41.3 per cent.

Thus the artificial cooling of the vapour, as was to be expected, increased the proportion of ammonium cyanate in the sublimate. Since the rate of heating might be expected to have an influence on the proportion of cyanic acid that would escape polymerisation, the following two experiments were made. Hantzsch has shown that cyanuric acid may be accurately titrated with sodium hydroxide solution, using phenolphthalein as indicator; it then behaves as a monobasic acid,  $\text{H}(\text{H}_2\text{C}_2\text{N}_3\text{O}_3)$ .

*Expt. 5.*—Carbamide heated very slowly, vapour not artificially cooled.

Sublimate = 0.0786.

$N/10\text{-AgNO}_3$  = 3.8 c.c.;  $\text{NH}_4\text{OCN}$  = 29 per cent.

Residue = 2.44 dissolved in water.  $N\text{-NaOH}$  = 2 c.c. Cyanuric acid = 10.57 per cent.

*Expt. 6.*—Carbamide heated very rapidly, as in *Expt. 5*.

Sublimate = 0.0955.

$N/10\text{-AgNO}_3 = 5.6$  c.c.;  $\text{NH}_4\text{OCN} = 35.18$  per cent.

Residue = 2.34.  $N\text{-NaOH} = 2.6$  c.c. Cyanuric acid = 14.33 per cent.

Whilst the polymerisation increases with the rate of heating, more cyanic acid is able to escape during the rapid heating, and hence the larger proportion of ammonium cyanate in the sublimate.

*Expt. 7.*—Biuret (2 grams) heated in test-tube until fluid commenced suddenly to thicken. Vapour artificially cooled.

Sublimate = 0.066.

$N/10\text{-AgNO}_3 = 4.7$  c.c.;  $\text{NH}_4\text{OCN} = 42.7$  per cent.

*Expt. 8.*—Biuret heated as above. Sublimate examined under microscope had characteristic fern-leaf-like formation (due to  $\text{NH}_4\text{OCN}$ ); the tube was now immersed to the neck in boiling water for a few minutes; the sublimate changed in appearance, and under the microscope was seen to consist of well-defined, broad-angled prisms. The solution of the crystals in water gave no precipitate with silver nitrate; some of the solution gave, with nitric acid in excess, characteristic crystals of carbamide nitrate. A similar result can be obtained with carbamide; the sublimate in the first instance, if dissolved in water, gives a copious precipitate with silver nitrate; after warming and then dissolving in distilled water a solution is obtained, which gives at most only a faint opalescence with silver nitrate. As both experiments can be performed in a few minutes, they form the subject of an interesting and instructive lecture demonstration to support the theories put forward. Further experiments are in progress over a more extended series of conditions.

#### *Examination of the Gaseous Products Evolved during the Decomposition of Carbamide by Heat.*

*Expt. 9.*—Five grams of finely powdered and well-dried carbamide were heated in a dry test-tube (2.5 cm. by 18 cm.), provided with a delivery tube dipping to the bottom of 50 c.c. of absolute alcohol contained in a flask immersed in ice-cold water. The carbamide was heated rapidly until the liquid became suddenly opalescent, indicating separation of cyanuric acid, whilst the tube was maintained in an almost horizontal position. A crystalline precipitate formed in the alcoholic solution, whilst the latter contained much free ammonia. The solution was poured off from the crystals, which were rapidly washed with a small quantity of fresh alcohol.

The solution of the crystals in water, and also the alcoholic solution, gave the following reactions:

VOL. CIII.

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(1) Addition of calcium chloride solution—no immediate precipitate in the cold; slight opalescence after ten minutes; a copious precipitate of calcium carbonate on warming.

(2) A portion of each solution was heated in a test-tube immersed in boiling water for five minutes, and then cooled; on addition of calcium chloride a faint opalescence was obtained, which was not sensibly increased by warming.

This last result could not be obtained if either ammonium carbamate or carbonate \* was present in the crystals or in the alcoholic solution; the absence of a precipitate of calcium carbonate in the second case being due to the disappearance of the ammonium cyanate by its conversion into carbamide on heating.

*Expt. 10.*—Carbamide was heated as before; the gas evolved was collected over mercury after expulsion of all the air; 50 c.c. of gas so obtained was found to be completely dissolved by 2 c.c. of water, and the solution gave no opalescence with calcium chloride.

These results prove that ammonia and cyanic acid are the only volatile products, and no carbon dioxide is present when dry carbamide is heated.

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### CVIII.—*The Synthetical Preparation of the d-Glucosides of Sitosterol, Cholesterol, and Some Fatty Alcohols.*

By ARTHUR HENRY SALWAY.

It has recently been shown (T., 1913, 103, 399) that phytosterol glucosides are of frequent occurrence in plants. These substances, which have been designated phytosterolins, vary to some extent in composition and character according to the plant from which they have been isolated. In many cases the phytosterolin appears to consist of sitosterol-*D*-glucoside,  $C_{27}H_{45}O \cdot C_6H_{11}O_5$ , whilst in other instances it seems to be a mixture of this substance with the glucoside of stigmasterol,  $C_{30}H_{49}O \cdot C_6H_{11}O_5$ . In order to obtain additional information regarding the character of these natural substances, it was deemed of importance to attempt the synthesis of a phytosterol glucoside, and compare its properties with those of the naturally occurring phytosterolins. The phytosterol

\* This would be formed if water accompanied the carbon dioxide and ammonia.

chosen for this purpose was sitosterol,  $C_{27}H_{46}O$ , since the latter can be prepared in comparatively large quantities from wheat germ, and is uncontaminated with stigmasterol when obtained from this source. It was converted into the glucoside by treatment with bromoacetoglucose in ethereal solution in the presence of dry silver oxide. The sitosterol-*d*-glucoside thus obtained was found to possess properties closely resembling the phytosterolins, and there is no doubt that the substances previously designated ipuranol, cluytanol, and trifolialol consist almost entirely of sitosterol-*d*-glucoside.

In addition to the synthesis of sitosterol-*d*-glucoside, the glucosides of cholesterol, myricyl alcohol, ceryl alcohol, and cetyl alcohol have been prepared. These glucosides have not hitherto been found in nature, but it appears probable, in the light of recent observations, that the glucosides of the fatty compounds, ceryl, cetyl, and myricyl alcohols, do occur in small quantities in plants, and that they have not hitherto been isolated owing to the difficulty attending their separation. The synthesis of these glucosides was of importance, since a knowledge of their properties would greatly facilitate the future examination of plants for the presence of such substances.

It was also intended to prepare the glucoside of the so-called *ischolesterol*, and a commercial specimen of the latter was procured for the purpose. The material was found, however, to be a very impure mixture of substances, since it contained considerable quantities of cholesterol and carnaubyl alcohol,  $C_{24}H_{38}O$ , and no substance agreeing with the *ischolesterol* of Schulze and his pupils (*J. pr. chem.*, 1873, [ii], 7, 163; 1874, [ii], 9, 325; 1882, [iii], 25, 159), or of Darmstädter and Lifschütz (*Ber.*, 1898, 31, 97), could be isolated from it. It may furthermore be noted in this connexion that the statements of the above-mentioned authors concerning the properties and composition of *ischolesterol* are so conflicting that further investigation of the subject is desirable.

The question whether the glucosides prepared in this investigation belong to the  $\alpha$ - or  $\beta$ -series has been left undecided on account of the fact that the insolubility of these substances in water renders the emulsion test for  $\alpha$ - and  $\beta$ -glucosides indecisive. Fischer and Helferich (*Annalen*, 1911, 383, 68) have shown, however, that in almost all cases the method of preparation of glucosides described by them, and adopted in the present investigation, leads to the formation of  $\beta$ -glucosides, so that the glucosides now obtained probably belong also to this series. In the case of ceryl-*d*-glucoside, however, it is of interest to note that the present author has isolated two distinct modifications, which may possibly represent the  $\alpha$ - and  $\beta$ -forms of the glucoside, although no definite evidence to this effect has been obtained.

The formation of two modifications of ceryl-*d*-glucoside,  $C_{27}H_{55}O \cdot C_6H_{11}O_5$ , is of some interest in connexion with an observation of E. Fischer and Helferich (*loc. cit.*) regarding the properties of cetyl-*d*-glucoside,  $C_{16}H_{33}O \cdot C_6H_{11}O_5$ . These investigators showed that cetyl-*d*-glucoside melts indefinitely, beginning to change at  $78^\circ$  and finally melting at about  $145^\circ$ ; it now seems probable, in view of the results obtained with ceryl-*d*-glucoside, that this behaviour is due to the presence of two modifications. In order to ascertain whether this were the case, cetyl-*d*-glucoside was prepared, but although it was found to possess the properties described by Fischer and Helferich, it was not possible to separate the two modifications.

#### EXPERIMENTAL.

##### I. *Sitosterol-d-glucoside*, $C_{27}H_{45}O \cdot C_6H_{11}O_5$ .

The sitosterol required for the preparation of this compound was obtained from wheat-germ (compare Burian, *Monatsh.*, 1897, **18**, 551). The fatty oil from 50.8 kilos. of the latter was hydrolysed with an excess of potassium hydroxide in the presence of alcohol, and the resulting soap solution extracted repeatedly with ether. The ethereal solution was then evaporated, and the residue crystallised from ethyl acetate, when the sitosterol was obtained in colourless needles, melting at  $138^\circ$ . The amount of pure substance isolated from 50.8 kilos. of wheat germ was 130 grams (compare Pickard, *T.*, 1908, **93**, 1928). It possessed the specific rotation  $[\alpha]_D -32.2^\circ$  ( $c=2.9$  with chloroform), and on analysis gave results agreeing well with the formula  $C_{27}H_{46}O$ .

In order to ascertain whether the material was quite free from stigmasterol, it was acetylated, and the acetyl derivative treated with bromine according to Windaus and Hauth's method (*Ber.*, 1906, **39**, 4378), but a negative result was obtained, thus showing the absence of stigmasterol.

For the conversion of sitosterol into its glucoside, 15 grams of anhydrous substance and 15 grams of pure bromoacetoglucose were dissolved in dry ether and shaken continuously for eight hours with freshly precipitated, dry silver oxide. The mixture was then filtered, a little dilute nitric acid having been previously added to coagulate the silver oxide and facilitate the filtration, after which the ethereal filtrate was washed, dried, and evaporated. The residue was next crystallised once from alcohol to remove a small amount of soluble by-product formed from the bromoacetoglucose. The substance thus obtained then consisted of a mixture of tetra-acetyl-sitosterol-*d*-glucoside and unchanged sitosterol, and could not be resolved into its components by direct fractional crystallisation. It

was therefore dissolved in hot alcohol, and the solution digested for about a minute with an excess of potassium hydroxide. In this manner the acetyl groups of the glucoside were eliminated without affecting the remaining part of the molecule, and the free glucoside, which is only sparingly soluble in hot alcohol, was deposited. This was collected, washed with hot alcohol, and purified by crystallisation from a mixture of pyridine and alcohol, when it separated in rosettes of small, colourless needles. When heated in a capillary tube, the substance begins to soften at about 270°, and melts and decomposes at 295–300°. The yield of pure substance amounted to 4 grams:

0.1023 gave 0.2721 CO<sub>2</sub> and 0.0960 H<sub>2</sub>O. C = 72.2; H = 10.4.

C<sub>35</sub>H<sub>56</sub>O<sub>6</sub> requires C = 72.3; H = 10.2 per cent.

*Sitosterol- $\beta$ -glucoside*, C<sub>27</sub>H<sub>45</sub>O·C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>, is insoluble in water and only sparingly soluble in alcohol, ether, chloroform, or benzene. It dissolves readily in pyridine, and can be easily crystallised from this solvent in admixture with alcohol. It yields the characteristic colour reaction of the phytosterols when dissolved in acetic anhydride and chloroform, and a drop of concentrated sulphuric acid then added. When heated with aqueous hydrochloric acid in the presence of amyl alcohol it is readily resolved into its components, sitosterol and dextrose.

*Tetra-acetylsitosterol- $\beta$ -glucoside*, C<sub>35</sub>H<sub>43</sub>O·C<sub>6</sub>H<sub>7</sub>O<sub>5</sub>Ac<sub>4</sub>.—This substance was prepared by heating the glucoside for thirty minutes with an excess of acetic anhydride. The greater part of the latter was then removed by distillation, alcohol added to the residue, and the crystalline solid which separated then recrystallised from alcohol. It was thus obtained in colourless, glistening leaflets, melting at 166–167°:

0.1010 gave 0.2540 CO<sub>2</sub> and 0.0812 H<sub>2</sub>O. C = 68.6; H = 8.9.

C<sub>41</sub>H<sub>54</sub>O<sub>10</sub> requires C = 68.7; H = 8.9 per cent.

0.5694, made up to 20 c.c. with chloroform, gave  $\alpha_D = 1.618'$  in a 2-dm. tube, whence  $[\alpha]_D = 22.9^\circ$ .

*Tetra-acetylsitosterol- $\beta$ -glucoside* is very readily soluble in ether, chloroform, benzene, or hot alcohol, but only sparingly so in cold alcohol. It is immediately hydrolysed in the presence of alkali hydroxides with regeneration of the glucoside.

*Tetra-benzoylsitosterol- $\beta$ -glucoside*, C<sub>27</sub>H<sub>35</sub>O·C<sub>6</sub>H<sub>5</sub>O·Bz<sub>4</sub>.—In order to obtain this compound, sitosterol- $\beta$ -glucoside was dissolved in pyridine, and the solution gently warmed for about a minute with an excess of benzoyl chloride. The mixture was then poured into alcohol, when the benzoyl derivative separated as a flocculent precipitate. This was collected and purified by crystallisation from



chloroform and alcohol, when it was obtained in slender, colourless needles, melting at  $198^{\circ}$ :

0.1075 gave 0.2988  $\text{CO}_2$  and 0.0721  $\text{H}_2\text{O}$ .  $\text{C} = 75.8$ ;  $\text{H} = 7.5$ .

$\text{C}_{61}\text{H}_{72}\text{O}_{10}$  requires  $\text{C} = 75.9$ ;  $\text{H} = 7.5$  per cent.

0.4733, made up to 20 c.c. with chloroform, gave  $\alpha_D + 0^{\circ}52'$  in a 2-dcm. tube, whence  $[\alpha]_D + 18.3^{\circ}$ .

Tetrabenzoylsitosterol-*d*-glucoside is readily soluble in chloroform, ethyl acetate, or benzene, but sparingly so in alcohol.

The above-described properties of sitosterol-*d*-glucoside closely resemble those of the naturally occurring phytosterolins, and it is evident that the substances previously designated ipuranol, cluytanol, and trifolanol consist almost entirely of sitosterol-*d*-glucoside.

## II. Cholesterol-*d*-glucoside, $\text{C}_{27}\text{H}_{45}\text{O} \cdot \text{C}_6\text{H}_{11}\text{O}_5$ .

The cholesterol employed in the preparation of the above glucoside melted at  $146$ – $147^{\circ}$ , gave on analysis results agreeing with the formula  $\text{C}_{27}\text{H}_{46}\text{O}$ , and possessed an optical rotation of  $[\alpha]_D - 40.3^{\circ}$  ( $c = 2.1$  in chloroform).

Five grams of cholesterol and 5 grams of bromoacetoglucose, dissolved in ether, were shaken for eight hours in the presence of dry silver oxide, and the product of the reaction was examined in the manner described in connexion with the preparation of sitosterol-*d*-glucoside. The cholesterol-*d*-glucoside thus obtained was purified by crystallisation from dilute pyridine, when it was deposited in minute, colourless needles, which began to soften about  $270^{\circ}$ , and completely melted at  $285^{\circ}$ . The yield of glucoside amounted to 2 grams:

0.0704 gave 0.1864  $\text{CO}_2$  and 0.0651  $\text{H}_2\text{O}$ .  $\text{C} = 72.2$ ;  $\text{H} = 10.3$ .

$\text{C}_{33}\text{H}_{56}\text{O}_6$  requires  $\text{C} = 72.3$ ;  $\text{H} = 10.2$  per cent.

The properties of cholesterol-*d*-glucoside are very similar to those of sitosterol-*d*-glucoside. It is very sparingly soluble in alcohol, chloroform, or ether, but readily so in pyridine or hot amyl alcohol. It yields the characteristic cholesterol colour reactions.

*Tetra-acetylcholesterol-d-glucoside*,  $\text{C}_{27}\text{H}_{45}\text{O} \cdot \text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$ .—This substance was obtained by heating the glucoside with acetic anhydride for half an hour. On removing the greater part of the latter and adding alcohol to the residue, a crystalline acetyl derivative was deposited, which was recrystallised from alcohol, and obtained in colourless needles, melting at  $159$ – $160^{\circ}$ :

0.0882 gave 0.2222  $\text{CO}_2$  and 0.0707  $\text{H}_2\text{O}$ .  $\text{C} = 68.7$ ;  $\text{H} = 8.9$ .

$\text{C}_{41}\text{H}_{64}\text{O}_{10}$  requires  $\text{C} = 68.7$ ;  $\text{H} = 8.9$  per cent.

0.1822, made up to 20 c.c. with chloroform, gave  $\alpha_D - 0^{\circ}26'$  in a 2-dcm. tube, whence  $[\alpha]_D - 23.8^{\circ}$ .

III. *Myricyl-d-glucoside*,  $C_{30}H_{61}O \cdot C_6H_{11}O_5$ .

Five grams of myricyl alcohol were shaken for eight hours with a dry ethereal solution of bromoacetylglucose (5 grams) in the presence of dry silver oxide (5 grams). The mixture was then filtered, the filtrate evaporated, and the solid residue, which contained the desired tetra-acetylmyricyl-*d*-glucoside mixed with unchanged myricyl alcohol, was dissolved in a mixture of equal parts of hot benzene and alcohol. On cooling, the greater part of the myricyl alcohol separated and was collected, whilst the tetra-acetyl derivative of the glucoside remained in the filtrate. The latter was subsequently heated for a very short time (about one minute) with an excess of alcoholic potassium hydroxide, and the glucoside, which separated on cooling, collected and washed with cold alcohol. It was purified by dissolving in hot chloroform and precipitating the glucoside from solution by the addition of ether. This product was then crystallised from hot alcohol, when it separated in small, colourless plates, melting at  $99^\circ$ . The yield of pure glucoside amounted to about 10 per cent. of the myricyl alcohol employed in the reaction:

0.1000 gave 0.2642  $CO_2$  and 0.1078  $H_2O$ .  $C=72.1$ ;  $H=12.0$ .

$C_{30}H_{61}O_6$  requires  $C=72.0$ ;  $H=12.0$ , per cent.

*Myricyl-d-glucoside* is insoluble in water, sparingly soluble in ether or chloroform, but readily so in pyridine or hot alcohol. It could only be obtained in one modification, thus differing from the glucoside of ceryl alcohol.

*Tetra-acetylmyricyl-d-glucoside*,  $C_{30}H_{61}O \cdot C_6H_7O_5 \cdot 4Ac$ .—This compound was obtained by heating the glucoside with acetic anhydride for some time, then removing the greater portion of the latter by distillation and adding alcohol to the residue. The precipitate of acetyl derivative thus obtained was crystallised from a mixture of ethyl acetate and alcohol, when it separated in small, colourless leaflets, melting at  $78-79^\circ$ :

0.1010 gave 0.2533  $CO_2$  and 0.0972  $H_2O$ .  $C=68.4$ ;  $H=10.7$ .

$C_{34}H_{56}O_{10}$  requires  $C=68.6$ ;  $H=10.5$  per cent.

0.1542, made up to 20 c.c. with chloroform, gave  $\alpha_D = 0.010$  in a 2-dm. tube, whence  $[\alpha]_D = 10.8^\circ$ .

Tetra-acetylmyricyl-*d*-glucoside is readily soluble in ether, chloroform, or benzene, but only sparingly so in cold alcohol.

IV. *Ceryl-d-glucoside*,  $C_{27}H_{55}O \cdot C_6H_{11}O_5$ .

The preparation and isolation of this compound were effected in a manner precisely similar to that adopted in the preparation of

myricyl-*D*-glucoside. The glucoside was obtained, after being crystallised from methyl alcohol, in small, hexagonal plates, melting at 94°. The yield of pure substance amounted to about 10 per cent. of the ceryl alcohol employed:

0.1460 gave 0.3808 CO<sub>2</sub> and 0.1560 H<sub>2</sub>O. C=71.1; H=11.9.  
C<sub>35</sub>H<sub>66</sub>O<sub>6</sub> requires C=71.0; H=11.8 per cent.

*Ceryl-D-glucoside* was found to exist in two modifications, the one melting at 94°, as described above, whilst the other melts at 135°. The latter was obtained by dissolving the former in hot chloroform, when glistening leaflets of the modification of high melting point immediately separated from the hot solution. If the latter is recrystallised from alcohol, it is more or less transformed into the modification of lower melting point. The glucoside melting at 135° was analysed, with the following result:

0.0871 gave 0.2263 CO<sub>2</sub> and 0.0928 H<sub>2</sub>O. C=70.9; H=11.8.  
C<sub>35</sub>H<sub>66</sub>O<sub>6</sub> requires C=71.0; H=11.8 per cent.

*Tetra-acetylceryl-D-glucoside*, C<sub>27</sub>H<sub>50</sub>O·C<sub>6</sub>H<sub>7</sub>O<sub>5</sub>Ac<sub>4</sub>.—This compound was prepared in the manner described in connexion with the preparation of tetra-acetylmyricyl-*D*-glucoside. It crystallised from a mixture of alcohol and ethyl acetate in small, colourless leaflets, melting at 85–87°:

0.0758 gave 0.1883 CO<sub>2</sub> and 0.0696 H<sub>2</sub>O. C=67.8; H=10.2.  
C<sub>41</sub>H<sub>74</sub>O<sub>10</sub> requires C=67.8; H=10.2 per cent.

0.2010, made up to 20 c.c. with chloroform, gave  $\alpha_D$  = -0°17' in a 2-dm. tube, whence  $[\alpha]_D$  = -14.1°.

#### V. *Cetyl-D-glucoside*, C<sub>16</sub>H<sub>33</sub>O·C<sub>6</sub>H<sub>11</sub>O<sub>5</sub>.

This glucoside has already been described by Fischer and Helferich (*loc. cit.*). In the present investigation it was prepared by the method of these authors, but a more expeditious way of isolating the product was adopted. Five grams of cetyl alcohol were shaken for eight hours in dry ethereal solution with bromo-acetoglucose (5 grams) and dry silver oxide (5 grams). The mixture was then filtered to remove the silver, the ethereal filtrate evaporated, and the residue from the latter hydrolysed in alcoholic solution by heating for about a minute with an excess of potassium hydroxide. Water was then added to the alcoholic liquid, and the precipitated solid extracted with ether. On washing the ethereal solution with water and thus removing the alcohol contained in it, the glucoside separated as a flocculent precipitate, which was collected and crystallised from chloroform. It was thus obtained in small, colourless needles, which began to soften at 78°, and completely melted at about 150°. It yielded an acetyl derivative,

melting at 71—73°, and was thus found to possess the properties previously ascribed to it. The glucoside could not be separated into modifications of definite melting point as in the case of ceryl-*d*-glucoside.

*Tetrabenzoylcetyl-d-glucoside*,  $C_{16}H_{33}O \cdot C_6H_5O_2Bz_4$ .—This derivative of cetyl-*d*-glucoside, not hitherto described, was prepared by heating the glucoside with benzoyl chloride for a few minutes in the presence of pyridine. On adding alcohol and keeping the mixture for some time, the benzoyl compound separated in clusters of silky needles, melting at 65°:

0.0963 gave 0.2600  $CO_2$  and 0.0653  $H_2O$ .  $C=73.2$ ;  $H=7.3$ .

$C_{30}H_{60}O_{10}$  requires  $C=73.2$ ;  $H=7.2$  per cent.

0.2380, made up to 20 c.c. with chloroform, gave  $\alpha_D + 0^\circ 22'$  in a 2-dm. tube, whence  $[\alpha]_D + 15.4^\circ$ .

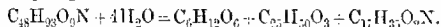
*Tetrabenzoylcetyl-d-glucoside* is readily soluble in ether, chloroform, or benzene, but dissolves sparingly in alcohol.

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## CIX.—*Oxidation of Sphingosine and the Isolation and Purification of Cerebrone.\**

By ARTHUR LAPWORTH.

SPHINGOSINE was isolated from decomposition products of brain-lipoids by Thudichum ("Die chemische Constitution des Gehirns," Tübingen, 1901), and its relations to one of these, namely, "cerebrone," was established by the work of Thierfelder and his pupils, who showed that the latter compound undergoes hydrolysis with acids, yielding molecular proportions of galactose, cerebronic acid, and sphingosine:



Cerebronic acid was recognised as a hydroxycarboxylic acid, whilst sphingosine proved to be a mono-acidic base, yielding stable salts with mineral acids (Thierfelder, *Zeitsch. physiol. Chem.*, 1904, **43**, 21; 1905, **44**, 366; Kitawaga and Thierfelder, *ibid.*, 1906, **49**, 286).

Between 1906 and the end of 1911 nothing of note was published dealing with the chemistry of cerebronic acid or sphingosine, and in 1910 the author was asked by Prof. Lorrain Smith to assist in his studies of brain lipoids, in connexion with the question of the

\* Abstracts, I., 1913, **29**, 151, 175.

processes of fatty degeneration (compare Lorrain Smith and Mair, *J. Path. Bact.*, 1910, **15**, 122; 1911, **16**, 131; also Lapworth, *ibid.*, 1911, **16**, 255). The method described by Lorrain Smith and Mair for the quantitative isolation of cerebrone from chloroform extract of brain was examined by the author with the object of preparing this lipoid on a large scale and simultaneously investigating the exact nature of cerebronic acid and sphingosine. Having corroborated the more important points established by Thierfelder, the author proceeded, in conjunction with Prof. W. H. Perkin, to investigate the constitution of cerebronic acid; the latter compound was analysed, its methyl ester prepared and purified and the percentage of methoxyl determined by Zeisel's method, with results entirely in harmony with Thierfelder's conclusions. Simultaneously the author was examining the properties of sphingosine, and in particular its behaviour towards oxidising agents, and observed that the base was converted by boiling nitric acid into a variety of products, including succinic acid and a mixture of acids having the properties of those of the fatty series, some being readily, and others but slightly volatile in steam. Suspecting that most of these were secondary products, attempts were made to isolate the highest of these by the use of a mild oxidising agent, and partial success was met with when chromic acid was used, it being observed that the acid product was free from the more volatile constituents formerly present.

At this juncture the papers by Levene and Jacobs (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxix) and by Thomas and Thierfelder appeared (*Zeitsch. physiol. Chem.*, 1912, **77**, 202). The first-named authors practically established the character of sphingosine as a dihydroxy-derivative of a primary, unsaturated amine; Thomas and Thierfelder confirmed by independent observations the fact that sphingosine yielded a triacetyl derivative. A request was tendered by Thierfelder to be allowed for some years to work in sole possession of the field of investigation of the brain-cerebrosides, but to this Levene and Jacobs, with considerable reason, did not accede.

The experiments in the author's and Prof. Perkin's laboratories were for the most part abandoned temporarily, in view of the considerable strides made by Levene and Jacobs and by Thierfelder, and it was decided for the time being simply to complete the practical modifications of Lorrain Smith and Mair's method of cerebrone-extraction on a large scale and to identify the fatty acid of highest molecular weight present in the oxidation mixture from cerebrone, and of which no mention had so far been made in any publication by other workers.

*Preparation of Pure Cerebrone on a Large Scale.*

The fresh brain is partly dried by soaking in spirit, and, when firm, is passed through a mincing machine and exhaustively extracted with boiling methyl alcohol. The alcoholic extracts, with any material they may deposit, are united, and solvent removed by distillation until they contain about 5–10 per cent. of residue not volatile at 100°, when about 0.5 gram of solid phenolphthalein per litre is added. A cold saturated solution of barium hydroxide in methyl alcohol is very slowly dropped into the boiling liquid until the latter assumes a faint red colour, indicative of alkalinity, and permanent for half an hour; this results in the deposition of much phosphatic material as a viscid, coherent mass, the presence of which renders the subsequent operations difficult (compare Lapworth, *J. Path. Bact.*, 1911, 15, 255) and therefore the supernatant solution is finally decanted into another flask, the small quantity of cerebrone which is retained in the viscid residue being extracted, if necessary, with successive small quantities of boiling methyl alcohol.

The united methyl-alcoholic liquors, if allowed to cool, deposit a white, easily filterable mass, consisting of cholesterol, mixed with cerebrone which obstinately retains phosphatides. These phosphatides cannot, in the author's experience, be removed by any process other than hydrolysis. Having tried hydrolysis with aqueous baryta and found it unsatisfactory from the point of view of simplicity in manipulation on a large scale, and destructive of much cerebrone when prolonged, as appears usually necessary, the author has based his subsequent procedure on the observations of Lorrain Smith and Mair (*J. Path. Bact.*, 1910, 15, 122, 1911, 16, 131), which were published prior to the paper of Loening and Thierfelder, who also advocated the use of boiling acetone as purifying agent (*Zeitsch. physiol. Chem.*, 1912, 77, 202, *et seq.*), but had evidently overlooked the earlier work.

The decanted liquor and washings are raised once more to boiling, and finely powdered barium oxide or hydroxide is shaken in, every precaution being taken to avoid the formation of clots protecting the oxide; in all, 1 gram of BaO is used for every 6 grams of residue not volatile at 100° previously estimated to be present in the original alcoholic extract. The boiling is continued for ten to twelve hours, when the bulk of the solvent is removed by distillation. To the still moist residue in the flask is added a mixture of equal volumes of chloroform and methyl alcohol (5 c.c. of this mixture for every gram of "residue not volatile at 100°"), and a pinch of solid phenolphthalein, the whole raised to boiling,

glacial acetic acid added drop by drop until all trace of red colour in solution and solid has been discharged; the mixed solvent is then removed by distillation.

Cerebrone and cholesterol are now easily freed from sparingly soluble phosphatic acids and barium salts by extraction and recrystallisation from hot methyl alcohol, filtration being resorted to only at the beginning and the end of these operations; the first-named substances are then separated from one another by extraction with ether, when the cerebrone remains undissolved.

If phosphatides are still present in the cerebrone, the latter may be subjected to continuous extraction with boiling acetone, as recommended by Lorrain Smith and Mair (*loc. cit.*), but if the addition of the powdered baryta has been made so cautiously as to avoid the formation of lumps at the beginning of the hydrolysis, only traces of phosphatide will be found.

It may be worth while to state that the author has never observed cerebrone in a solid-crystalline form, although many specimens presented that appearance both to the naked eye and when examined with a microscope in polarised light with crossed nicols. As is also the case with sphingosine, very thin, plate-like forms often separate; these are birefringent, and bend in straight folds, thus producing the appearance of needles, especially in polarised light. In every case, however, the dry material, when heated, gradually became less firm, and finally quite fluid, no break being observed until the birefringence and viscosity of the fluid-crystalline substance disappeared at about 200°, so that the so-called "melting point" is only the clearing point of the opalescent "crystalline" fluid. This is but a corroboration and extension of the conclusions of Lorrain Smith and Mair (*Proc. Path. Soc.*, 1910, 8), who were the first to recognise the fluid-crystalline characters of cerebrone and sphingosine as they usually appear, and the true character of the so-called melting point of cerebrone. The author has had the advantage of their experience and advice in his observations on the nature of the seeming crystals of these two compounds, and the facts are worthy of wider attention than they appear to have received.

#### *Preparation of Sphingosine.*

Cerebrone, prepared as above, and free from phosphorus, was hydrolysed by hot 3 per cent. aqueous hydrochloric acid for twenty-four hours. The resulting insoluble mixture of cerebronic acid and sphingosine hydrochloride was rapidly washed with water, then dissolved in hot methyl alcohol, and mixed with excess of a saturated solution of sodium hydroxide in the same solvent. Sodium cerebrionate separated on cooling, and was removed by filtration,

the filtrate diluted with four times its bulk of water and extracted with ether; the latter was washed several times with water containing 15 per cent. of methyl alcohol, evaporated and dried at 100°. The residue, which was mainly sphingosine, was extracted with cold spirit, the resulting clear solution nearly neutralised with sulphuric acid, and the precipitated sphingosine sulphate crystallised from alcohol.

#### *Oxidation of Sphingosine.*

Sphingosine sulphate, prepared and purified as above, was dissolved in glacial acetic acid and cautiously oxidised with successive small quantities of chromium trioxide at the lowest temperature required to cause slight effervescence; oxidation was completed with excess of trioxide at 100°, when the liquid was diluted with water, and excess of chromium trioxide reduced by a stream of sulphur dioxide. A current of steam was then used to remove most of the acetic acid, the receiver being changed when solid matter appeared in the condenser. The first portions of solid which passed over were collected, dried, and distilled in a vacuum, and were found to melt at 38·5–40°.

As distillation of the acid slackened, the green liquid in the flask was cooled, extracted with ether, and the latter evaporated. A green residue was obtained, which was decomposed readily by concentrated hydrochloric acid, yielding a green solution and a white solid, which was found to be identical with the volatile acid, and had evidently been retained as chromium salt.

Unfortunately some of the acid was lost before the total weight was determined, but the yield would evidently have been considerable, and 2·3 grams were finally isolated in purified state from 8 grams of sphingosine sulphate.

#### *Identification of the Acid.*

The collected acid was dried and distilled; it boiled constantly at 136–137/100 mm., and successive small fractions of the distillate all melted between 38·5 and 40·5°:

0·2790 gave 0·7440 CO<sub>2</sub> and 0·3020 H<sub>2</sub>O. C=72·7; H=12·0.

C<sub>13</sub>H<sub>26</sub>O<sub>2</sub> requires C=72·8; H=12·2 per cent.

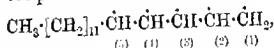
For the determination of its equivalent, a solution of sodium in methyl alcohol was standardised by means of pure stearic acid, with litmus as indicator. 0·2620 Gram of stearic acid required 10·45 c.c., whilst 0·1302 gram of the acid under examination required 6·90 c.c., under precisely similar conditions, to yield a solution with the same tint. The equivalent of the acid was therefore 212, that required for a monobasic acid, C<sub>13</sub>H<sub>26</sub>O<sub>2</sub>, being 214.



As these properties were very similar to those attributed to *n*-tridecylic acid, a sample of the latter was made from myristic acid by converting the latter in its  $\alpha$ -bromo- and  $\alpha$ -hydroxy-derivative successively and oxidising the latter with potassium permanganate in acetone. The product was identical in all respects with the acid obtained from sphingosine, and had no influence on its melting point. The substances, separately or mixed, presented, on a slide beneath a cover slip, precisely the same appearance when fused and allowed to solidify, forming clear areas with sharply defined edges; in all three cases, too, the materials when examined in convergent polarised light exhibited in most regions one axis of a biaxial interference figure emerging obliquely and at apparently the same angle to the normal.

In view, however, of the general tendency of fatty acids to form mixed crystals, thus rendering complete identification less simple than usual, a sample of the acid from sphingosine was brominated in a closed tube in presence of phosphorus pentachloride, the product decomposed by boiling with anhydrous formic acid and the  $\alpha$ -bromo-derivative crystallised from the same solvent. A portion of this  $\alpha$ -bromo-acid was next converted by Le Sueur's method (T., 1905, 87, 1905) into the  $\alpha$ -hydroxy-acid. This bromo-compound and the hydroxy acid melted at 29.5–30° and at 76–77° respectively, whilst Le Sueur (*loc. cit.*, *et seq.*) gives 30.5° and 78° respectively for the corresponding derivatives of tridecylic acid, an agreement which, considering the small quantity of acid brominated (less than 1 gram), was sufficiently close fully to establish the identity of the oxidation product of sphingosine as tridecylic acid.

Whilst it is obvious that much experimental work remains to be done before the exact constitution of sphingosine is established, yet it would seem probable, having regard to the fact that straight carbon chains are characteristic of most of the simpler brain substances that the complex:



is present in this base.

Evidence as to the position of the ethylenic linking should be obtainable by examining the oxidation products of Levene and Jacob's dihydrosphingosine. If, for example, the double linking unites the atoms numbered (4) and (5), then oxidation of the reduced base should furnish *n*-quindecylic acid, and doubtless these workers will be able to decide this question.

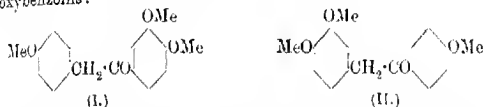
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# CX.—*Synthesis of Unsymmetrical Derivatives of Deoxybenzoin.*

By JOHN CANNELL CAIN, JOHN LIONEL SIMONSEN, and  
CLARENCE SMITH.

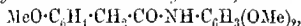
In a recent paper (Cain and Simonsen, T., 1912, 101, 1061) it was shown that santalin dimethyl ether,  $C_{17}H_{18}O_6$ , on oxidation with potassium permanganate, yields a mixture of anisic and veratric acids, and it appeared to be of interest therefore in connexion with the elucidation of the constitution of santalin, to synthesise a series of compounds which might be expected to furnish the above acids on oxidation.

In the present paper is described the synthesis of two trimethoxy-deoxybenzoinis:



The starting point for the preparation of *β-keto-α-4-methoxyphenyl-β-3:4-dimethoxyphenylethane* (I) was *p*-methoxyphenylpyruvic acid (Dakin, *J. Biol. Chem.*, 1910, 8, 17; Wakeman and Dakin, *ibid.*, 1911, 9, 150), which on oxidation with hydrogen peroxide yielded *p*-methoxyphenylacetic acid,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ ; the chloride of this, when condensed with veratrole by means of aluminium chloride, gave the desired substance (I).

The substituted deoxybenzoin obtained in this way gives with hydroxylamine an *oxime*,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot C(:NOH) \cdot C_6H_3(OMe)_2$ , and when the latter is treated with phosphorus pentachloride, *p*-methoxyphenylaceto-3:4-dimethoxyanilide,



is produced.

By a similar series of reactions *β-keto-β-4-methoxyphenyl-α-3:4-dimethoxyphenylethane* (II) was obtained. 3:4-Dimethoxyphenylpyruvic acid (Kropp and Decker, *Ber.*, 1909, 42, 1184) was oxidised to 3:4-dimethoxyphenylacetic acid, the chloride of which was condensed with anisole to the required compound (II) of which the *oxime* was prepared.

## EXPERIMENTAL.

### *β-Keto-α-4-methoxyphenyl-β-3:4-dimethoxyphenylethane* (I).

*p*-Methoxyphenylpyruvic acid,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot CO_2H$ , was prepared by heating the lactone of *α*-benzoylamino-*p*-methoxy-

cinnamic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C} \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagdown \quad \diagup \\ \text{N} = \text{C}_{\text{Ph}} \end{smallmatrix}$ , with aqueous potassium hydroxide, as described by Wakeman and Dakin (*loc. cit.*), but the acid was isolated in a different manner from that adopted by these authors.

The lactone (55 grams) was mixed with potassium hydroxide (64 grams) in water (600 c.c.), and heated on the sand-bath under reflux until no further odour of ammonia could be detected (about five hours). The liquid was cooled, acidified, and the oily mixture of acids extracted with ether. In order to separate the benzoic and pyruvic acids, the mixture was esterified and fractionally distilled under 15 mm. pressure. After the ethyl benzoate had passed over, the temperature rose rapidly, and *ethyl p-methoxyphenylpyruvate* distilled with considerable decomposition at about  $190^\circ$ . For identification it was converted into its *semicarbazone*, which separated from alcohol in colourless needles, melting at  $152-153^\circ$ :

0.1108 gave 16.0 c.c.  $\text{N}_2$  at  $32^\circ$  and 753 mm.  $\text{N} = 15.4$ .

$\text{C}_{13}\text{H}_{17}\text{O}_4\text{N}_3$  requires  $\text{N} = 15.1$  per cent.

In order to obtain the free acid the ester (5 grams) was hydrolysed on the water-bath with alcoholic potassium hydroxide (3 grams KOH), the alcohol removed, and, on acidifying, the acid separated as a semi-solid mass. This was ground with hot benzene, which removed the coloured impurity, leaving the acid as a chalky, white mass. After crystallisation from a mixture of ethyl acetate and benzene, the properties of the acid agreed with those described by Wakeman and Dakin.

*Preparation of p-Methoxyphenylacetic Acid.*—In order to prepare this acid, the mixture of benzoic acid and *p*-methoxyphenylpyruvic acid was not isolated, but was directly oxidised by hydrogen peroxide in the following manner.

The alkaline solution of the acids obtained by the hydrolysis of the lactone (90 grams) with potassium hydroxide was extracted with ether to remove a trace of oily impurity, and treated gradually with hydrogen peroxide (30 c.c. of "perhydrol" diluted with 300 c.c. of water). The oxidation takes place rapidly, and the solution was kept well cooled. After remaining overnight the solution was filtered and acidified, the mixture of acids extracted with ether, and the latter were converted into their esters in the usual manner. On distilling under 7 mm. pressure, ethyl benzoate passed over first, and then *ethyl p-methoxyphenylacetate*, which was readily obtained pure, and boiled at  $138-140^\circ$  (yield, 30 grams). On hydrolysis, *p*-methoxyphenylacetic acid was isolated in iridescent plates, melting at  $85-87^\circ$ .

When *p*-methoxyphenylacetic acid is treated with phosphorus pentachloride, it is converted into its *chloride*, which is an oil having an odour like that of benzoyl chloride and boiling at 143°/10 mm.:

0.1868 gave 0.1496 AgCl. Cl=19.4.

$C_9H_9O_2Cl$  requires Cl=19.2 per cent.

*p*-Methoxyphenylacetyl chloride (10 grams) was dissolved in carbon disulphide (50 c.c.), and after the addition of veratrole (15 grams), aluminium chloride (15 grams) was slowly added. When the vigorous reaction which took place had subsided, the mixture was heated on the water-bath for three hours. The deep red aluminium compound which had separated was decomposed in the usual manner, and the carbon disulphide and unchanged veratrole were removed by means of steam. On cooling, the trimethoxydeoxybenzoin (I) separated as a reddish-brown, crystalline mass. It was collected, well washed with sodium carbonate solution and water, and purified by crystallisation from alcohol, from which it separates in bunches of slender needles, melting at 118°:

0.1657 gave 0.4308  $CO_2$  and 0.0335  $H_2O$ . C=70.9; H=6.3.

0.1372 „ 0.4308  $CO_2$  „ 0.0318  $H_2O$ . C=71.1; H=6.6.

$C_{17}H_{15}O_4$  requires C=71.3; H=6.3 per cent.

*β-Keto-α-4-methoxyphenyl-β-3:4-dimethoxyphenylethane* (I) is readily soluble in benzene, ethyl acetate, chloroform, or hot alcohol, but only sparingly so in light petroleum or cold alcohol. It gives no colour with ferric chloride. When treated with bromine, substitution readily takes place, but a mixture of bromo-derivatives seems to be formed, and so far no crystalline compound has been isolated.

The *oxime*,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot C(=NOH) \cdot C_6H_3(OMe)_2$ , was readily obtained when the trimethoxybenzoin was dissolved in alcohol and heated with an alcoholic solution of hydroxylamine hydrochloride and potassium hydroxide on the water-bath for some hours. On pouring into water an oil separated, which rapidly solidified. For analysis it was crystallised from alcohol, from which it separated in well-developed prisms, melting at 143°:

0.1207 gave 0.2981  $CO_2$  and 0.0690  $H_2O$ . C=67.4; H=6.3.

$C_{17}H_{15}O_4N$  requires C=67.8; H=6.3 per cent.

A careful examination of the mother liquors showed that not a trace of the isomeric oxime was formed.

When this oxime, dissolved in a mixture of benzene and ether, was treated with phosphorus pentachloride in the usual manner, the Beckmann rearrangement took place, and *p*-methoxyphenylaceto-3:4-dimethoxyanilide,  $MeO \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_3(OMe)_2$ , was formed. This was isolated in the usual manner, and purified by

crystallisation from alcohol, when it separated in prismatic needles, melting at 147—148°:

0.1204 gave C 60 c.c. N<sub>2</sub> at 33° and 763 mm. N = 5.3.

C<sub>17</sub>H<sub>19</sub>O<sub>4</sub>N requires N = 4.6 per cent.

When hydrolysed with concentrated hydrochloric acid, the anilide yielded *p*-methoxyphenylacetic acid and veratrylamine (m. p. 80—82°; platinichloride, yellow needles, m. p. 227—228°).

*β*-Keto-*β*-4-methoxyphenyl- $\alpha$ -3:4-dimethoxyphenylethane (II).

The alkaline solution resulting from the hydrolysis of the lactone of  $\alpha$ -benzoylamino-3:4-dimethoxycinuamic acid and containing 3:4-dimethoxyphenylpyruvic acid (Kropp and Decker, *loc. cit.*) was gradually treated with 200 c.c. of 3 per cent. hydrogen peroxide, the flask being cooled by water during the oxidation. After keeping for about twenty hours, the pale yellow solution was filtered and acidified. The pasty mixture of acids thus obtained was extracted with ether, and the crude acids (54 grams) remaining after evaporation of the ether were esterified in the usual manner. The mixture of esters was isolated and fractionated under diminished pressure. After ethyl benzoate had distilled over at 117—120°, 48 mm., the temperature rose rapidly, and *ethyl* 3:4-dimethoxyphenylacetate passed over at 199—200°. By redistillation the ester (15 grams) was obtained as a colourless liquid, boiling at 191°/25 mm.

3:4-Dimethoxyphenylacetic acid was obtained by hydrolysing the ester with alcoholic potassium hydroxide. Its properties corresponded with those given by Pictet and Finkelstein (*Ber.*, 1909, 42, 1984).

3:4-Dimethoxyphenylacetyl chloride (Pictet and Finkelstein, *loc. cit.*, p. 1985) was dissolved in 70 c.c. of dry carbon disulphide, 20 grams of anisole were added, and the mixture was treated slowly with 20 grams of aluminium chloride. A vigorous reaction soon commenced, which was moderated by cooling the flask in water. When the reaction had subsided, the mixture was heated on the water-bath for four hours. Ice and ice-cold water were then gradually added to the cooled mixture, which was well shaken and treated with 10 c.c. of concentrated hydrochloric acid. The reddish-black additive compound slowly decomposed, yielding a yellowish-brown solid. After the carbon disulphide and excess of anisole had been removed by means of steam, the reddish-brown residue was collected, washed with water, and ground twice with *N*-potassium hydroxide. The yellow residue (11 grams) was separated from the dark red solution, washed with water, dried in a vacuum, and crystallised twice from 96 per cent. alcohol and once from benzene.

The product of the reaction was thus obtained in colourless needles (4.5 grams), melting at  $138^{\circ}$ :

0.3153 gave 0.8238  $\text{CO}_2$  and 0.1760  $\text{H}_2\text{O}$ .  $\text{C}=71.3$ ;  $\text{H}=6.2$ .

$\text{C}_{17}\text{H}_{18}\text{O}_4$  requires  $\text{C}=71.3$ ;  $\text{H}=6.3$  per cent.

*$\beta$ -Keto- $\beta$ -4-methoxyphenyl- $\alpha$ -3:4-dimethoxyphenylethane* is extremely soluble in boiling benzene, and readily so in boiling 96 per cent. alcohol; in the cold solvents it is only sparingly soluble. It does not develop a coloration with concentrated alcoholic sodium hydroxide, but dissolves in concentrated sulphuric acid with a yellow colour.

The oxime,  $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}_2\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , was prepared by treating 0.71 gram of the substance just described, dissolved in 50 c.c. of 96 per cent. alcohol, with three equivalents of hydroxylamine hydrochloride and an excess (2 grams) of sodium hydroxide dissolved in water. After the mixture had been heated on the water-bath for two hours, the alcohol was removed by distillation, water was added to the residue, which was then acidified with dilute sulphuric acid. The precipitate was extracted with ether, the ether evaporated, and the oily residue, after two crystallisations from 96 per cent. alcohol, was obtained in colourless needles, melting at  $100-101^{\circ}$ :

0.1316 gave 5.2 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 776 mm.  $\text{N}=4.7$ .

$\text{C}_{17}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{N}=4.6$  per cent.

The authors express their thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the expense of the above investigation.

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### CXI.—*The Estimation of Small Quantities of Lead.*

By ALFRED VINCENT ELSDEN and JOHN FIRTH STANSFIELD.

WILKIE (*J. Soc. Chem. Ind.*, 1909, **28**, 636) states that lead in presence of a sufficiency of ferric iron is completely precipitated by ammonia. This has been confirmed, and it occurred to the authors that this property might form a convenient method for the separation and estimation of lead in small quantities in solution, since, having concentrated the lead in the precipitate of ferric hydroxide, it only remains to separate the two metals. After

solution of the precipitate in acid, the separation could, of course, be effected either by means of hydrogen sulphide or by evaporation with sulphuric acid, but a more rapid and equally accurate method has been devised.

It was at first hoped to effect the separation by precipitation of the iron in acid solution either as basic acetate or as basic formate, but many experiments under varying conditions of acidity, concentration, etc., have shown that a satisfactory separation of iron from lead cannot be obtained by this means. It was found that the more acid the solution the more complete was the separation, but eventually a point was reached when the solution was too acid for the complete precipitation of the iron, whilst the iron precipitate still carried down some lead.

Attention was then given to the precipitation of lead as molybdate. Brearley (*Chem. News*, 1898, **78**, 203), and later Brearley and Ibbotson ("Analysis of Steel Works Materials"), give some details of the precipitation of lead as molybdate, but with reference to quantities larger in general than those contemplated by the present authors. It was ascertained that even quantities as small as 2 or 3 milligrams of lead in a volume of 50 to 100 c.c. of solution could be accurately precipitated and weighed as molybdate, as will be seen from the following results, the lead being dissolved in about 75 c.c. of solution:

Lead added.	Lead found.
0.0252	0.0254
0.0680	0.0629
0.0020	0.0021

In the presence of ferric iron lead cannot be estimated as molybdate directly, since free mineral acid interferes with the precipitation, and in weak acetic acid solution iron will be co-precipitated.

The authors have found, however, that if the iron is first reduced to the ferrous condition the lead can be precipitated directly as molybdate in weak acetic acid solution without precipitation of iron, and this even when the iron is in relatively very much larger quantity than the lead. A single precipitation usually gives too high a result, but by redissolving and reprecipitating the lead molybdate the results are satisfactory, as the figures on p. 1041 show.

The detailed procedure for the estimation of small quantities of lead in solution is as follows.

To the solution is added at least ten times as much iron (as ferric chloride solution of known concentration) as there is likely to be lead present. After mixing thoroughly, ammonia is added in excess, and the solution boiled and filtered. The precipitate is

THE ESTIMATION OF SMALL QUANTITIES OF LEAD. 1041

Iron added.	Lead added.	Lead found.	Ratio Fe : Pb.
0.1000	0.0010	0.0011	100 : 1
0.0500	0.0020	0.0022	30 : 1
0.1000	0.0020	0.0022	50 : 1
0.1000	0.0020	0.0022	50 : 1
0.1000	0.0030	0.0030	33 : 1
0.1000	0.0040	0.0042	25 : 1
0.1000	0.0040	0.0041	25 : 1
0.1000	0.0050	0.0052	20 : 1
0.2000	0.0060	0.0061	33 : 1
0.1500	0.0070	0.0071	21 : 1
0.1500	0.0080	0.0083	19 : 1
0.2000	0.0100	0.0102	20 : 1

dissolved in 10—20 c.c. of hot concentrated hydrochloric acid, and the filter washed thoroughly with boiling water until the combined filtrate and washings reach a volume of about 75 c.c. Ammonia is then added to the solution, conveniently from a burette, until a slight permanent precipitate is produced.  $N/2$ -Hydrochloric acid is then added to the extent of 2 c.c. for every 0.0100 gram of iron used, with a minimum of 10 c.c.; 0.2 gram of sodium sulphite crystals are then added for every 0.0100 gram of iron, with a minimum of 1 gram, and the solution warmed until reduction is effected. Without boiling off the excess of sulphur dioxide, 10—20 c.c. of ammonium acetate solution (10 per cent.) are added, the solution heated to the boiling point, and finally 10—20 c.c. of ammonium molybdate solution (5 per cent.) are added slowly and with agitation of the liquid. After boiling for a short time the precipitate is filtered rapidly through a close textured paper, and washed two or three times with boiling water.

The precipitate is dissolved from the paper in 10 c.c. of hot concentrated hydrochloric acid, and the paper washed thoroughly with boiling water to a total volume of not more than 50 c.c. A few drops of tartaric acid solution (5 per cent.) and litmus solution are added, after which concentrated ammonia is added from a burette until the liquid is neutral. The solution is then acidified with a few drops of  $N/2$ -hydrochloric acid, and, after addition of a few c.c. of ammonium acetate solution, boiled for a short time. The precipitate is collected, washed with hot water, ignited with the paper, and weighed.

With regard to the influence of the presence of other elements on the precipitation of lead molybdate, Brearley (*loc. cit.*) has shown that a large number of metals do not interfere if certain precautions are taken. The present authors have investigated the influence of tin, antimony, and phosphorus on the procedure described above. If present in solution with the lead they are largely, if not completely, carried down by the iron precipitate. The method of dealing with the mixed precipitate has then to be modified, and it



## 1042 THE ESTIMATION OF SMALL QUANTITIES OF LEAD.

is desirable to separate the iron and the phosphorus by means of hydrogen sulphide in hydrochloric acid solution. The tin and antimony are then separated from the lead by means of ammonium sulphide in the usual manner. The remaining lead sulphide may be conveniently dissolved in hydrochloric acid containing bromine, and estimated as molybdate as already described. The following results were thus obtained:

Iron added.	Tin added.	Antimony. added.	Phosphorus added.	Lead added.	Lead found.
0.0500	0.0050	0.0050	0.0050	0.0040	0.0042
0.0500	0.0050	0.0050	0.0050	0.0050	0.0052
0.6500	0.0050	0.0050	0.0050	0.0060	0.0062

The authors believe that this method of separation and estimation of lead will be found capable of wide application, especially in those cases where small amounts of lead have to be separated from solution.

It may also be applied to the estimation of lead in many non-ferrous alloys, and in such cases, when the amount of lead is small, it has advantages as to speed and accuracy over the usual method of evaporation with sulphuric acid. The methods were compared in the case of a sample of brass, and of phosphor-bronze. The metals were dissolved in nitric acid, and the tin removed by filtration in the usual way. For determination of the lead as sulphate, the filtrate from the tin was evaporated with sulphuric acid, and the precipitate treated in the customary manner. For the estimation of the lead by the "iron-molybdate" method, to the filtrate from the tin was added 0.0500 gram of iron as ferric chloride and then ammonia in excess. The precipitate containing the lead and the iron was treated as described above, and the following results were obtained:

	Lead by sulphate method. Per cent.	Lead by "iron-molybdate" method. Per cent.
Brass (containing a little tin) .....	0.72	0.78
Phosphor-bronze.....	0.56	0.61

It will be noticed that the ordinary sulphate method gives results rather lower than those obtained by the "iron-molybdate method." In view of the appreciable solubility of lead sulphate, this was to be expected.

In conclusion, the authors desire to express their thanks to Mr. G. T. Holloway, to whom they are indebted for the alloys on which the above experiments were carried out.

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# CSII.—*The Spontaneous Crystallisation of Solutions of Potassium Chloride, Bromide, and Iodide.*

By BERNARD MOUT JONES and POPATHAL GOVINDIAL SHAH.

IN the investigation of the spontaneous crystallisation of solutions of the nitrates of potassium, rubidium, and caesium, one of the authors had observed (Jones, T., 1908, **93**, 1739) a relation between the extents of the metastable regions in aqueous solutions of these salts having a common anion. The work recorded below was undertaken with a view to determine whether in the case also of similar salts with a common cation any similar relation exists. The salts chosen, namely, potassium chloride, bromide, and iodide, were suitable for the purpose, as they all crystallise in the anhydrous condition and in the cubic system; they are, further, moderately soluble, and the viscosity of their supersaturated solutions should not offer serious hindrance to spontaneous crystallisation.

The work was begun and almost finished before that of Young on the mechanical stimulus to crystallisation (*J. Amer. Chem. Soc.*, 1911, **33**, 148) had come to our notice. Young's work affords strong evidence that no "metastable limit" exists; its apparent existence depends on the fact that in the experiments of Miers, Hartley, Jones, and others to determine the supersolubility curves of various solutions, the amount of mechanical stimulus afforded by shaking the solutions with hard substances (glass or garnet) has coincided with a "transitional" value. By plotting the temperatures of crystallisation against the energies of the shocks employed to induce crystallisation in water, benzene, and fused hydrated calcium chloride, curves of a hyperbolic character were obtained, which indicated that during a certain small range of temperature—the "transitional" region—shocks of considerably varying intensity would bring about crystallisation. Above this region the curve is asymptotic to the energy axis, indicating that a very large additional shock is necessary to raise the temperature of crystallisation by a small amount; below, the curve is asymptotic to the temperature axis, indicating that the supercooled liquid or solution is in a state very sensitive to shock, in which crystallisation is brought about by very small stimuli. The supersolubility curves are explained by Young as corresponding with these "transitional" regions; and so far as it goes the explanation appears to accord well with the facts. It is interesting that the "transitional" region found by Young for pure water lies in the neighbourhood of  $-0.6^{\circ}$ , the value obtained for the point of spontaneous crystallisation of ice by the shaking method.

Young's explanation of the supersolubility curves cannot, however, be considered complete, for although the intensity of the stimulus applied may be a large, perhaps the main, factor in bringing about crystallisation, it is likely that other, as yet undetermined, influences are at work, perhaps those of the nature suggested by Hartley and Thomas (T., 1906, 89, 1031). For if the intensity of the shock were the only factor to be considered, it is difficult to understand why in such closely similar salts as the nitrates of potassium, rubidium, and caesium, the supersolubility curve should be coincident with the solubility curve in the last case, and at an average distance of  $4^{\circ}$  and  $1^{\circ}$  in the two others; or, as is shown in the present paper, the corresponding values for the chloride, bromide, and iodide of potassium should be  $10^{\circ}$ ,  $12^{\circ}$ , and  $3^{\circ}$ . It would also be a curious coincidence if in all cases investigated by the shaking method, varying in character from Glauber's salt dissolved in water to triphenylmethane dissolved in benzene and comprising "metastable regions" varying in extent from nothing to 35 Centigrade degrees, the investigators should always have chosen just those conditions of mechanical stimulus which correspond with the "transitional" regions of Young. It would be expected that for substances of widely differing character the stimuli necessary to produce crystallisation and corresponding with the "transitional" region should also vary widely. This, indeed, Young has shown to be the case. It might not unreasonably be expected, then, that in some cases at least among those investigated by the shaking method, where the stimuli employed were all of the same order of magnitude, the "transitional" stimulus would have been greater than that actually employed.

Again, assuming that Young's curves, which are based on three points only in every case, represent the real relation between the energy of the stimulus and the temperature of crystallisation, it is seen that the "transitional" region covers a range of temperature of several degrees. It would be expected, then, that the observed temperatures of crystallisation obtained by the shaking method should also vary through this range. This has not been found, the observed temperatures almost always agreeing closely, even over wide ranges of temperature and concentration, within a few tenths of a degree, in spite of the fact that no attempts were made to keep constant the vigour of the shaking. In the present investigation the rapidity and violence of the shaking were purposely varied through a considerable range.

That other than purely mechanical factors enter into the problem is indicated by the fact that if the solubility-temperature coefficient of the salt is positive, the supersolubility curve runs closely parallel

to the solubility curve with a tendency to diverge from it at high temperatures and concentrations; whereas if the coefficient is negative ( $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), the supersolubility curve converges towards the solubility curve with increasing temperature, that is, decreasing concentration.

It would appear, then, justifiable to conclude that no specifically "metastable" region exists within which spontaneous crystallisation (that is, without the presence of crystal nuclei) *cannot* take place. At the same time, however, the supersolubility curves do mark a somewhat sudden change in properties in the supercooled liquids or supersaturated solutions. They do not mark a "metastable limit," yet they indicate a remarkably sharp change in conditions from a state (*labile*) where the tendency is for crystallisation not to occur except under very violent stimuli, to a state (*metastable*) in which with moderate shaking, whereby the hindering effect of viscosity is probably largely obviated, separation of the solid phase will *invariably* take place within a very short time. Young's explanation of the supersolubility curves does not diminish their practical importance in defining the boundary between these two states, nor does it take into account those factors, other than purely mechanical, which would appear to play some part in the phenomenon. Whether the explanation advanced by Hartley and Thomas account for these other factors cannot as yet be said to be proved. It does at least invoke the aid of the kinetic theory, which in a problem of this nature it would be unwise to ignore completely. The influence of time as a factor in bringing about the "accident of crystallisation" is also doubtless not to be neglected.

In the present investigation on the chloride, bromide, and iodide of potassium, all three salts have given well-defined supersolubility curves under the conditions of experiment, slow cooling and moderate agitation and mechanical shock. The supersolubility curves for both the ice and the salt phases have been traced.

#### EXPERIMENTAL.

The method used was the same as that employed in previous investigations (Hartley, Jones, and Hutchinson, T., 1908, **93**, 825; Jones, T., 1908, **93**, 1739; 1909, **95**, 1672). The tubes were shaken by various means: by hand, by an electric-bell shaker, by a mechanical shaker worked by a hot-air motor, or by a highly-g geared hand-turned machine. The energy of the shaking was then widely varied, but the manner and vigour of the shaking seemed to have little or no effect on the temperature of crystallisation. The shape and material of the tube also appeared to be without influence on the temperature of crystallisation. The bulbs of the tubes were

blown as thin as was consistent with safety to allow of their contents assuming the temperature of the bath as rapidly as possible. The same results were obtained whether ordinary or Jena glass was used, but perhaps the crystallisation phenomena were most definite in tubes of Jena glass with conical bulbs, this shape giving somewhat greater opportunity for mechanical shock during shaking. Mechanical friction or stimulus was promoted by adding small crystals of garnet (about 2 mm. across); this made the phenomenon of crystallisation much more definite than was the case in the absence of solid substances. Fragments of Jena glass were first used, since, being amorphous, they could have no inoculating effect, but they were found to be unsatisfactory, as they broke up on shaking, giving rise to minute fragments, the presence of which hindered the observation of the first appearance of the crystals, which they closely resembled. Since in all cases the solutions had to be cooled well below the saturation point before crystallisation could be induced, it may be supposed that the garnets, too, although crystalline, had but very small, if any, inoculating effect.

The influence of the rate of cooling of the bath on the temperature of crystallisation was investigated. It was found that so long as the rate was kept reasonably slow, not more than  $1^{\circ}$  in ten minutes, crystallisation always occurred at the same temperature within a few tenths of a degree (compare Jaffé, *Zeitsch. physikal. Chem.*, 1903, **43**, 585). More rapid cooling caused a lowering of the apparent temperature of crystallisation, due probably to the fact that the temperature fall within the bulb lagged somewhat behind that of the surrounding bath. Slower cooling up to about  $1^{\circ}$  in half an hour or more had no appreciable effect on the temperature of crystallisation. The rate generally employed was about  $1^{\circ}$  in fifteen minutes.

Every tube before cooling in the bath was heated in boiling water in order to get rid of all possible solid crystal nuclei. The time during which the tube was heated had apparently no influence on the crystallisation temperature so long as it was more than a certain minimum value of about ten to fifteen minutes, which appeared to be the time necessary to dissolve all traces of solid crystals. A tube heated for periods varying from twenty minutes to three hours would give the same crystallisation temperature at every determination.

The observation of Jaffé (*loc. cit.*), that "the temperature at which spontaneous crystallisation appears sinks very slowly and steadily with the number of times a tube is experimented with," was not confirmed in the present work. The contents of the same tube would crystallise at a definite temperature even after repeated

observations extending over four months. Jaffé, however, used neither solids to promote friction nor mechanical shaking, and his results are therefore perhaps hardly comparable with ours.

The separation of the salt phase from the solution almost always took place in the same way. One or two very small crystals, often visible only through a pocket lens, would appear, and these after a short time would multiply rapidly either at the same temperature or on cooling through one or two tenths of a degree. The detection of the first appearance of the crystals was often a matter of some difficulty, and sometimes of a little uncertainty, since even the garnets would occasionally give rise to very minute, colourless fragments easily confounded with minute salt crystals. They could be distinguished, however, by watching whether they grew or not on lowering the temperature. "Showers" of crystals were only rarely observed, and these only in the more concentrated solutions.

The influence of the solvent action of the water on the glass upon the temperature of crystallisation was investigated, and found to be very small. Two tubes of similar size and shape were made, one of Jena and the other of ordinary glass. Solutions of potassium chloride were prepared and sealed up in the ordinary way, and the crystallisation points determined immediately. They gave salt crystals at  $38.2^{\circ}$  and  $29.5^{\circ}$  respectively. On repeating the experiments four months later, they were found to be  $38.2^{\circ}$  and  $29.9^{\circ}$ . Similarly, a tube containing 4.12 parts of chloride to 100 of water gave ice at  $-3.8^{\circ}$  after four months, whilst a freshly prepared tube containing 3.99 parts of chloride gave ice at  $-3.6^{\circ}$ . The effect of the dissolution of the glass was evidently very small.

#### *Crystallisation of Potassium Chloride.*

Table I gives the highest temperatures at which potassium chloride crystallised from aqueous solutions of various strengths. The results

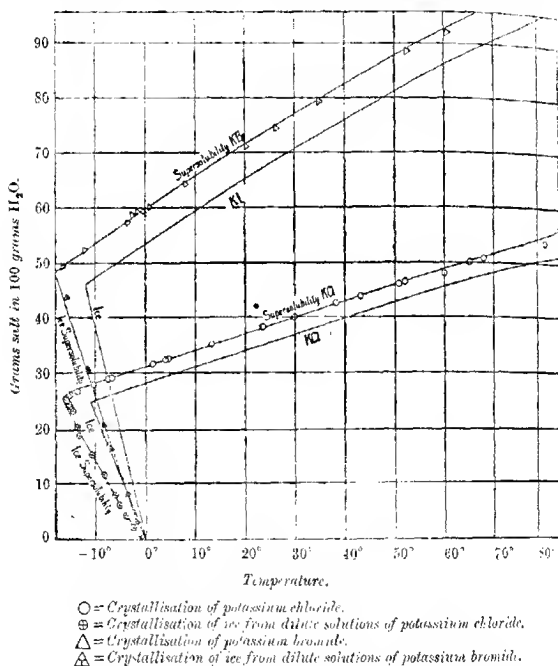
TABLE I.

Grams of potassium chloride in 100 grams of water.	Temperature of crystallisation of potassium chloride.	Grams of potassium chloride in 100 grams of water.	Temperature of crystallisation of potassium chloride.
54.69	$81.9^{\circ}$	35.55	$13.3^{\circ}$
51.03	$67.9$	32.75	$4.7$
50.33	$65.0$	32.54	$4.3$
48.32	$60.0$	31.81	$1.2$
46.63	$52.2$	29.08	$-6.5$
46.37	$50.9$	28.92	$-7.4$
44.02	$43.2$	27.93	$-10.2$
44.00	$43.2$	26.72	$-13.5$
42.94	$38.2$	25.97	$-14.9$
40.32	$29.9$	25.87	$-15.2$
38.65	$23.6$	25.51	$-15.5$

are plotted in Fig. 1, which shows both the solubility and supersolubility curves. The phenomenon of crystallisation was very definite, successive determinations often agreeing within one-tenth, and always within three or four tenths, of a degree. The supersolubility curve runs practically parallel to the solubility curve at an average distance from it of  $10^{\circ}$ .

FIG. 1.

*Solubility and supersolubility curves of potassium chloride and bromide in water.*



*Crystallisation of Ice from Solutions of Potassium Chloride.*—Table II shows the temperatures at which ice separates spontaneously from dilute solutions of potassium chloride. The tubes were at first shaken in a freezing mixture contained in a vacuum vessel, which enabled the crystallisation to be observed without removing the tube from the bath, the cooling being brought about by the addition

of ice or salt when necessary. It was not, however, easy in this way to secure a regular rate of cooling, nor to maintain the temperature uniform throughout the bath. It was therefore abandoned in favour of a well-stirred toluene bath surrounded by a freezing mixture of ice and salt. The production of the ice phase was quite a definite phenomenon, and the temperatures of crystallisation are seen to lie on a well-defined supersolubility curve (Fig. 1). The ice- and potassium chloride-supersolubility curves give rise to a hypertectic point at about  $-15.7^{\circ}$ . The region in the neighbourhood of the hypertectic point was thoroughly investigated, and a tube containing 25.51 grams of potassium chloride in 100 grams of water gave a mixture of ice and salt crystals at  $-15.7^{\circ}$ .

The temperature at which ordinary pure distilled water crystallised in tubes containing garnets was found to be  $-0.6^{\circ}$ , a value agreeing well with those previously obtained: Hartley, Jones, Hutchinson,  $-0.5^{\circ}$ ; Miers,  $-0.4^{\circ}$ ; Jones,  $-0.7^{\circ}$ .

TABLE II.

Grams of potassium chloride in 100 grams of water.	Temperature of crystallisation of ice.	Grams of potassium chloride in 100 grams of water.	Temperature of crystallisation of ice.
0.00	$-0.6^{\circ}$	18.77	$-13.0^{\circ}$
2.00	$-2.1$	20.40	$-13.5$
3.79	$-3.6$	23.44	$-14.4$
4.12	$-3.8$	24.09	$-15.1$
6.03	$-5.1$	24.30	$-15.3$
7.99	$-6.0$	24.96	$-15.5$
11.73	$-8.1$	25.19	$-15.7$
15.48	$-10.5$	25.51	$-15.7$

*Crystallisation of Potassium Bromide.*

The temperatures of spontaneous crystallisation of solutions of potassium bromide are given in table III, and are plotted in Fig. 1. The character of the phenomena was quite similar to that in the case of the chloride.

The supersolubility curve runs almost exactly parallel to the

TABLE III.

Grams of potassium bromide in 100 grams of water.	Temperature of crystallisation of potassium bromide.	Grams of potassium bromide in 100 grams of water.	Temperature of crystallisation of potassium bromide.
112.90	$107.0^{\circ}$	64.39	$8.1^{\circ}$
92.18	$60.1$	60.61	$0.9$
88.78	$52.6$	59.89	$-0.1$
79.85	$34.9$	59.61	$-1.3$
77.19	$30.5$	58.96	$2.3$
74.97	$26.2$	57.37	$3.5$
71.72	$20.2$	52.79	$-11.9$
67.61	$12.1$	49.60	$-16.4$



solubility curve at an average distance from it of about  $12^{\circ}$ . The data for both the ice and salt solubility curves at temperatures below  $0^{\circ}$  are contradictory and untrustworthy. In drawing the curves the average values given by Seidell have been adopted.

*Crystallisation of Ice from Solutions of Potassium Bromide.*

Table IV gives the temperatures of spontaneous crystallisation of ice from dilute solutions of the bromide; they are plotted on Fig. 1, where the ice- and salt-supersolubility curves are seen to intersect at the hypereutectic temperature of about  $-18^{\circ}$ , the solution then containing about 49 parts of salt to 100 of water.

TABLE IV.

Grams of potassium bromide in 100 grams of water.	Temperature of crystallisation of ice.	Grams of potassium bromide in 100 grams of water.	Temperature of crystallisation of ice.
0.00	-0.6°	21.00	-8.2°
3.12	-1.9	31.15	-11.3
8.17	-3.5	44.01	-15.3
16.49	-6.8		

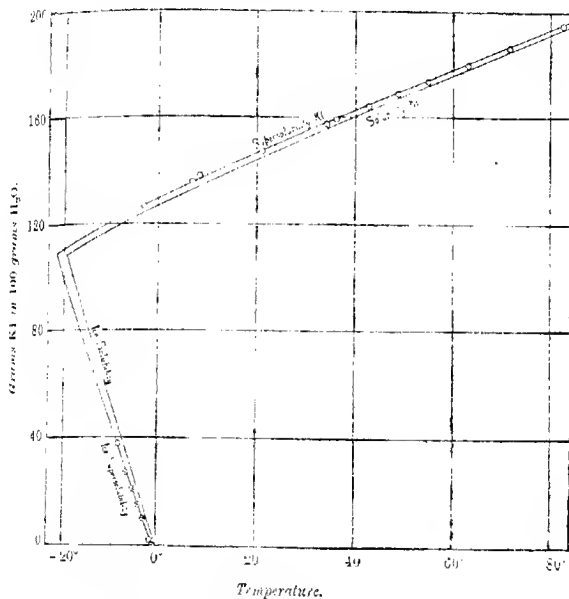
*Crystallisation of Potassium Iodide.*

In the case of the iodide the "metastable region" appears to be considerably smaller than in the case of the chloride and bromide, namely, about  $3^{\circ}$  as against  $10^{\circ}$  and  $12^{\circ}$ . This made the detection of the first crystals a matter of greater difficulty, since the "relief of supersaturation" on crystallisation was relatively much smaller. Moreover, the crystallisation was a comparatively slow process. The first crystals to appear were only visible through a lens, and always very few in number; they did not themselves grow rapidly, nor as a rule induce rapid crystallisation through the rest of the solution. It was often, in fact, necessary to lower the temperature a few tenths of a degree to make certain that the crystals would grow. Successive determinations of the temperature of first appearance of the crystals, however, gave quite concordant results. For example, tube No. VI (179.6 parts of potassium iodide to 100 parts of water) gave crystals at  $63.0^{\circ}$ ,  $63.0^{\circ}$ ,  $63.1^{\circ}$  in successive experiments; No. VII (173.7) gave crystals at  $54.7^{\circ}$ ,  $55.0^{\circ}$ ,  $55.0^{\circ}$ ; No. VIII (186.7) gave crystals at  $71.8^{\circ}$ ,  $71.7^{\circ}$ ,  $71.7^{\circ}$ ; No. XIII (141.7) crystallised between  $14.2^{\circ}$  and  $15.3^{\circ}$  (preliminary determination), at  $14.5^{\circ}$  (not at  $14.9^{\circ}$ ), at  $14.6^{\circ}$  (not at  $14.8^{\circ}$ ). All the tubes showed after heating that hydrolysis had taken place by the brown colour of the liberated iodine; and this was the more noticeable in the more highly concentrated solutions. The amount of chemical action was, however, probably not sufficient materially to affect the temperature of crystallisation.

The results are given in table V and plotted in Fig. 2, where the supersolubility curve is seen to be nearly parallel to the solubility curve. As in the case of the bromide, the ice- and salt-solubility curves given in the figure are based on rather discordant data.

FIG. 2.

*Solubility and supersolubility curves of potassium iodide in water.*



○ = Crystallisation of potassium iodide.

⊙ = Crystallisation of ice from dilute solutions of potassium iodide.

TABLE V.

Grams of potassium iodide in 100 grams of water.	Temperature of crystallisation of potassium iodide.	Grams of potassium iodide in 100 grams of water.	Temperature of crystallisation of potassium iodide.
195.3	82.7°	157.7	34.2°
186.7	71.7	147.2	21.1
179.6	63.1	145.9	19.5
173.7	55.0	141.7	14.6
169.2	48.9	138.0	9.4
164.3	43.0	135.7	7.0
159.3	36.2	126.9	-2.9

*Crystallisation of Ice from Solutions of Potassium Iodide.*—The results are given in table VI, and are plotted in Fig. 2. The ice and salt-supersolubility curves would seem to meet on prolongation at a hypertectic point of about  $-22^{\circ}$ , the solution at that temperature having a concentration of about 108.5 parts of salt to 100 of water.

TABLE VI.

Grams of potassium iodide in 100 grams of water.	Temperature of crystallisation of ice.	Grams of potassium iodide in 100 grams of water.	Temperature of crystallisation of ice.
0.00	$-0.6^{\circ}$	21.51	$-4.8^{\circ}$
1.94	$-1.3$	27.20	$-6.3$
10.18	$-2.8$	37.84	$-7.8$
15.30	$-3.9$		

The work was done in the laboratories of the Government and Forman Christian Colleges, Lahore, India.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, S. W.

### CXIII.—*The Chemical Nature of Some Radioactive Disintegration Products. Part II.*

By ALEXANDER FLECK, B.Sc.

SINCE the first part of this paper, describing the chemistry of a number of radioactive disintegration products, was written a short time ago, the subject has become of great theoretical importance, due to the elucidation of the general law governing the position of the radio-elements in the periodic table (A. S. Russell, *Chem. News*, 1913, **107**, 49; G. von Hevesy, *Physikal. Zeitsch.*, 1913, **14**, 49; *Phil. Mag.*, 1913, [vi], **25**, 390; K. Fajans, *Physikal. Zeitsch.*, 1913, **14**, 131; *Ber.*, 1913, **46**, 422; F. Soddy, *Chem. News*, 1913, **107**, 97; *Jahrb. Radioakt. Elektronik.*, 1913, **10**, 188). The work described in this paper is a continuation of that previously published, and deals with the chemistry of radium-A, thorium-D, and actinium-D, which were the only three substances of period of average life greater than three minutes the chemistry of which remained unknown. By means of a more powerful actinium preparation it has also been possible to confirm the previous conclusion as to the nature of actinium-B.

It was early shown in the work that will be described that thorium-D differs from lead in many respects (Fleck, *Chem. News*, 1913, **107**, 95), and this was the position when, from the general

theoretical laws referred to, it was predicted (Fajans, Soddy, *loc. cit.*) that the *D* members should be analogous to thallium. This prediction, both with regard to thorium-*D* and actinium-*D*, has been fully realised in the course of the work. Since the publication of the first part of the paper, Metzner (*Ber.*, 1913, 46, 979) has given details of experimental work, in which he shows that thorium-*D* is inseparable from thallium, and confirms the result (Fleck, *T.*, 1913, 103, 390) that bismuth and thorium-*C* are non-separable. Prior to the publication of Metzner, Soddy had, in a postscript to his paper, published the result, dealt with in this paper, that thorium-*D* may be quantitatively separated from the other members of the active deposit group by precipitating potassium platinichloride in the solution, thus establishing its analogy to thallium.

### *Radium-A.*

It was a matter of remark at an early stage in the experimental investigation that polonium remained the only radio-element with chemical properties not possessed by any other. The tables of Fajans and Soddy, however, show that there must be six other substances with chemical properties identical with those of polonium. Of these six, however, radium-*A* is the only one of period sufficiently long to be measured directly, and even in the case of this substance there are numerous difficulties to be overcome which are not met with in the case of the radio-elements previously studied. Only  $\alpha$ -rays can be used to determine the relative quantities of radium-*A*.  $\beta$ -Rays, from the radium-*C* produced, cannot be used because, before a deposit of radium-*A* can be dissolved, added to a solution of some substance, and that substance submitted to a chemical reaction and collected, from one to one and a-half minutes must elapse from the instant of withdrawal from the emanation, and in this time about 25 per cent. of the radium-*A* would have changed to radium-*B*. This quantity of radium-*B* would behave, of course, differently from radium-*A*, and what would be finally measured would be, by no means, the initial relative quantities of radium-*A*. It is, of course, impossible to measure relative quantities of a substance giving  $\alpha$ -rays, like radium-*A*, when distributed through weighable quantities of material owing to the absorption of the rays.

Another difficulty is that no matter how pure initially the radium-*A* may be, its radiation does not decay exponentially to zero, but decays for a number of minutes, after which the activity may remain constant or else rise to a maximum due to the accumulation of radium-*C*, before finally falling to zero with the period approaching that of radium-*B*. The result of this is that all experiments must be made and sufficient measurements taken within about six

minutes from the time of withdrawal of the active deposit from the emanation. Otherwise it is impossible to prove that it is actually radium-A that is being experimented on.

The first experiments that were made to attempt to confirm the view that radium-A and polonium would be identical were concerned with the volatility of these two substances. A copper foil, *A* (see Fig. 1),  $4 \times 1$  cm. in size, was allowed to remain in a hydrochloric acid solution of polonium, some of which was deposited on the copper foil. This foil, after washing and drying, was then laid on a stouter piece of copper foil *B*, of larger area, and with an opening just smaller than  $4 \times 1$  cm. On the top of the foil *A*, a third foil, *C*, rested, which was exactly similar in size to the foil *B*. On the top of the third foil, *C*, a fourth foil, *D*, of the same size as foil *A*, was placed. Foil *A* was then heated for fifteen or twenty seconds with a blow-pipe, which caused the polonium to volatilise and to condense mostly on the top foil *D*. The object in doing this was to get the polonium on a foil in the same physical state for the subsequent volatilisation experiment as the radium-A would

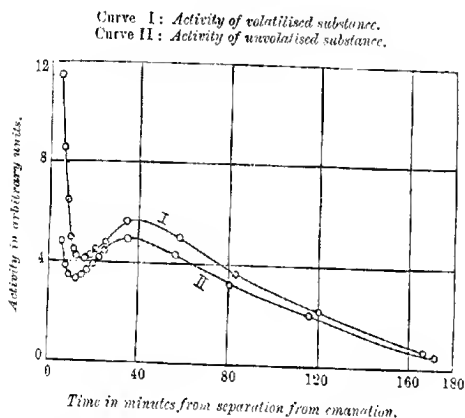
FIG. 1



be, both being deposited from the air. The top foil had a small hole bored in it, so that it could be hooked on to an insulated wire passing through the cork of the flask containing the radium emanation. The wire with the foil attached was then connected with the negative terminal of the 250 volt circuit, and then plunged into the emanation for five seconds. This foil having now radium-A on it besides volatilised polonium, took the place of foil *A*, and a fresh foil was placed at *D*, after which the former was heated for a few seconds with a blow-pipe, so that some polonium would be volatilised and some remain. The two foils were then immediately taken to an electroscope with a 0.0031 mm. thick aluminium base, and placed on a stand 3.5 cm. below the base. This distance was calculated so that the intervening air space and the thickness of the aluminium foil absorbed all the  $\alpha$ -rays from polonium, whilst the  $\alpha$ -rays from the active deposit alone would be measured in the electroscope. One pair of the curves obtained are shown in the accompanying figure (Fig. 2). The top curve, which was obtained from the volatilised substance, shows clearly that when the measurements were started it contained pure radium-A, whilst the bottom curve shows that the radium-A was not pure, but contains also the radium-B and -C which have accumulated during the short time that must elapse between removing the foil from the emanation and finishing the volatilisation. From the unvolatilised substance curve it is not possible to deduce any exact measure of the quantity of radium-A

present, but it can be said that it must be less than the value represented by the curve, since there is a quantity of radium-C present. The ratio of the two quantities of radium-A must therefore be greater than 2.042—the actual ratio of the activities. The relative quantities of polonium were measured the following day, when it was found that their ratio was 1.161, showing apparently that radium-A is more volatile. This difference, however, may not be real, but only apparent. Two elements are said to be non-separable when one cannot be taken away without the other from a uniform mixture of the two. It has to be borne in mind, however, that in this case the polonium is deposited a considerable time before the radium-A, and that it may diffuse into the copper foil,

FIG. 2.



from which it will not be so easily volatilised as the radium-A. Besides, it may be that we are working with two layers, although they are only of atomic thickness. If that is so it is natural that a greater fraction of the top layer, radium-A, would volatilise. It therefore seemed that this experiment should not be regarded as conclusive evidence that radium-A was more volatile than polonium.

The reason for the well-defined maximum, not usually observed, is that the ionisation due to radium-A is produced by the last half-centimetre of the range of that  $\alpha$ -particle, whilst the  $\alpha$ -particle of radium-C has a much longer range, and consequently the ionisation due to radium-C is relatively much greater than that due to radium-A. That is to say, that in the following equation  $\alpha$  has

$$3 \approx 2$$

been diminished with reference to  $\gamma$  by this experimental disposition. The equation for this curve is:

$$I = K\{ae^{-\lambda_1 t} + be^{-\lambda_2 t} + ce^{-\lambda_3 t}\},$$

where  $I$ =ionisation,  $K$ =constant,  $t$ =time from withdrawal of deposit from emanation,  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ =radioactive constants of radium-*A*, -*B*, and -*C* respectively; and

$$a = (0.23\alpha - 0.0292\beta + 0.0053\gamma),$$

$$b = (0.108\gamma + 0.0292\beta),$$

$$c = -0.114\gamma,$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are the numbers of ions produced in the electro-scope per atom in the disintegration of radium-*A*, -*B*, and -*C* respectively. Neglecting the number of ions produced by radium-*B*, since that number is very small compared with the numbers from radium-*A* and -*C*, the calculated time, from the instant of withdrawal of the active deposit from the emanation, required to reach the maximum value of the curve is 37.74 minutes. This is in good agreement with the experimental value of approximately 40 minutes.

The only radio-element which could be more volatile than polonium is thorium-*D*, which was known to resemble thallium (see p. 1058). In order to ascertain if radium-*A* was analogous to thorium-*D*, experiments were made with the precipitation of thallium with platinum chloride as platinichloride, and these showed that this precipitate brought down, in a solution of the radium active deposit, radium-*A* in excess of radium-*B* or -*C*. Yet with the complete precipitation of the thallium, only a small fraction—one part in every 14.5 parts of radium-*A*—is thus entrained. Radium-*A* is thus shown to be different from thallium and thorium-*D*.

Recourse was then had to electrolysis. The first attempts were made with the aid of a current from a battery, but finally the natural potential difference between a metal and a solution was used. By simply suspending a copper plate of about 23 sq. cm. area in a hydrochloric acid solution of polonium, and stirring it about in the liquid for one minute, an easily measurable quantity of polonium was deposited. Radium-*A* for all the following experiments was obtained by collecting the active deposit on a strip of magnesium ribbon, 3 cm. long, which was charged negatively on the 250 volt circuit. The ribbon, which was usually immersed in the emanation for about thirty minutes, and had thus a considerable quantity of radium-*B* and -*C* in addition to radium-*A*, was quickly removed from the emanation, dropped into a few c.c. of dilute hydrochloric acid, where it was completely dissolved in from ten to fifteen seconds, and the solution added to the polonium solution. The first experiments showed that, in addition to polonium, radium-*A* containing very little radium-*B* or -*C* was

deposited on the copper foil. In this work on radium-*A*, only those metals more electronegative than lead were used. It was not possible to get plates of arsenic, bismuth, or antimony, so that the experiments were confined to copper, silver, gold, and platinum. If lead or a more electropositive metal was used, then the whole active deposit was found on the metal.

The method was then used to see if the same proportion of radium-*A* as of polonium was deposited. This was done by dissolving the active deposit in the usual way in the polonium solution, and then placing simultaneously in the solution for one minute two plates of equal size, one of copper and the other of some other metal. The force driving the polonium and radium-*A* ions on to the copper plate will be different from the force driving them to the other plate, and thus we would expect, if polonium and radium-*A* were dissimilar substances, that, in general, the ratio of the two substances would be different on the two plates, and it might very easily happen that on some metal one was deposited quite readily, whilst the other was not at all deposited. In doing this experiment it is most essential that the two plates be kept electrically insulated from one another. If an electro-couple is formed, as, for instance, if the wires suspending the two plates come in contact with one another, or if one of the plates has an amalgamated surface, then both radium-*B* and -*C* are deposited. The results of the experiment are as follows:

Metals placed in solution.	Activity due to radium- <i>A</i> .	Ratio of activities due to radium- <i>A</i> .	Activity due to polonium.	Ratio of activities of polonium.
Copper .....	5.75	2.45	39.24	2.03
Silver .....	2.35		18.89	
Copper .....	10.4	1.1067	28.54	1.132
Gold .....	9.47		25.19	
Copper .....	7.84	1.57	50.29	1.81
Platinum .....	4.98		27.25	

The exact measure of radium-*A* on the gold plate was somewhat difficult to determine, and this is the meaning of the question mark.

The effects obtained are due to radium-*A*, since if the active deposit was dissolved as usual, and allowed to remain twenty minutes until radium-*A* has all disappeared, before a plate was immersed in the solution, only a very small quantity of radium-*B* and -*C* could be detected.

These experiments furnish another proof that radium-*A* is not similar to thorium-*D*. Von Lerch found that thorium-*D* was more difficult to deposit than thorium-*C*. It has been shown that thorium-*C* and radium-*C* have identical electrochemical and chemical



properties (von Hevesy, *Phil. Mag.*, 1912, [vi], 23, 628; Fleck, this vol., p. 393), and that therefore thorium-*D* is more difficult to deposit than radium-*C*. The preceding experiment shows that radium-*A* is much more easily deposited than radium-*C*, and therefore than thorium-*D*. There can be thus no similarity between thorium-*D* and radium-*A*.

The similarity of radium-*A* to polonium was confirmed by showing that, by precipitating a small quantity of bismuth oxychloride in a radium-*A* solution, more than 60 per cent. of the radium-*A* was actually measured on the filter paper, no allowance being made for the absorption of the  $\alpha$ -rays. Experiments like this one to ascertain what percentage of radium-*A* was precipitated were made by collecting the active deposit on two strips of magnesium ribbon of exactly the same size, placed in close contact with one another. One piece was then dissolved in acid, and the chemical reaction made, whilst the other was retained as a measure of the initial quantity of radium-*A* present.

Radium-*A* also remains in solution when lead is precipitated from an active deposit solution either as chloride or sulphate. This is shown by the fact that such a precipitate does not show any initial  $\alpha$ -ray decay, but, on the contrary, shows a steady increase of  $\alpha$ -ray activity.

All these experiments show that radium-*A* and polonium have chemically similar properties.

#### Thorium-*D*.

In the initial stages of the work, before anything was known of the chemistry of this substance, the experimental method was to work with pure thorium-*D* obtained by recoil (Hahn, *Ber. Dent. physikal. Ges.*, 1909, 11, 55). The thorium-*D* was recoiled from a highly polished brass plate, which had been kept negatively charged for twenty-four hours or more over a strongly emanating radiothorium preparation on to a platinum plate. The active material was then dissolved off by dropping the plate into boiling dilute nitric acid. Lead was then added to the solution, which also contained bismuth, and reprecipitated as lead sulphate or lead chloride. By these experiments it was seen that no thorium-*D*, or at most only a small fraction, was precipitated as sulphate or chloride, and hence that it was not analogous to lead.

The fact that all the known elements of atomic weight over 200, with the two exceptions of thallium and mercury, were similar to some of the radio-elements, suggested, even before the tables of Fajans and Soddy had been published, that thorium-*D* would perhaps be similar to one of these elements. Mercury seemed the

least likely, and it was soon found experimentally that thorium-*D* was not nearly so volatile as that element.

The experiment was therefore made of adding thallium to a solution of the thorium active deposit in equilibrium, and precipitating the thallium as platinichloride. This precipitate had an activity which decayed to zero with a period of half-value of 3.8 minutes. It was found that the initial  $\gamma$ -activity of the thallium precipitate, measured two minutes after precipitation with platinum chloride, was 54 per cent. of the activity obtained by precipitating the *B* and *C* members immediately after removal of the thallium and allowing the *D* member to come again into equilibrium. It is

FIG. 3.

Curve I:  $\beta$ -Ray curve of initially pure thorium-*C*.  
Curve II:  $\gamma$ -Ray curve of initially pure thorium-*C*.



thus shown that thorium-*D* is precipitated quantitatively with thallium platinichloride. It can also be precipitated completely with potassium platinichloride.

Other reactions show that thorium-*D* behaves like thallium, and not like potassium. It is precipitated completely by ammonium sulphide from a solution containing potassium, bismuth, thorium-*C*, and thorium-*D*. If the bismuth in such a solution is precipitated either as hydroxide or oxynitrate or as sulphide from an acid solution, the thorium-*D* remains dissolved. This is seen from such curves as are reproduced in Fig. 3. Curve No. 1 is obtained by measuring  $\beta$ -rays from bismuth oxynitrate precipitated from such a solution, and curve No. 2 is obtained by measuring the  $\gamma$ -radiation. It is observed that the  $\beta$ -radiation does not appear to rise from

zero to a maximum, whereas the  $\gamma$ -rays have a relatively much smaller initial value. This confirms the recent discovery that thorium-*C* gives  $\beta$ -rays but no  $\gamma$ -rays, whereas thorium-*D* gives both types (E. Marsden and C. G. Darwin, *Proc. Roy. Soc.*, 1912, **A**, 87, 17; O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1912, **13**, 390).

#### Actinium-B.

The opportunity was also taken of confirming the view (Fleck, T., 1913, 103, 394) that actinium-*B* was not only similar to lead, but non-separable from it, by making a series of fractional precipitations of lead sulphate from a solution containing lead and actinium active deposit. Four successive quantities of sulphuric acid gave precipitates Nos. 1, 2, 3, and 4, while the addition of alcohol to the filtrate from No. 4 gave precipitate No. 5.

Number of precipitate.	Weight of precipitate. Gram.	$\beta$ -Activity of precipitate 40 mins. from initial precipitation.	$\beta$ -Activity of precipitate per gram at that time.
1	0.3599	7.5	20.56
2	0.3732	8.1	21.66
3	0.1660	3.4	20.44
4	0.0296	0.58	19.60
5	0.0163	0.35	20.70

The activities were measured in an electroscope by divisions per minute, and the units are thus arbitrary.

The experiment shows that there is no alteration in the concentration of actinium-*B* in lead by such fractional treatment.

#### Actinium-D.

From the theoretical considerations already referred to, actinium-*D* should be analogous to thorium-*D* and to thallium. The method of

FIG. 4.



obtaining actinium-*D* in a pure condition was to suspend a needle of which all but a few millimetres were protected by a glass tube, in a tube containing the actinium preparation, and allow it to remain in this position negatively charged to 250 volts for a few hours. The needle was then removed, threaded with copper wire, passed through the tube *A* (Fig. 4), which was sealed with wax at the top. This tube was then placed in a small glass tube, containing a cylinder *M*, made of sheet magnesium, with which connexion could be made by a fine copper wire. The tube *AA* was then placed in the glass tube and exhausted through the side-tube *B*, whilst the needle was connected with the positive terminal, and the cylinder with the negative ter-

minimal of the 250 volt circuit. After not less than seven minutes the cylinder was dipped into dilute acid, and the recoiled actinium-*D* thus obtained in solution. Thallium nitrate was added to this solution, and then two successive quantities of hydrochloric acid, and finally ammonium sulphide. The results of this experiment are:

Number of precipitate.	Weight of thallium present. Gram.	$\beta$ -Activity of precipitate 5 mins. from start.	$\beta$ -Activity per gram at that time.
1	0.0900	5.0	55.6
2	0.0722	4.2	58.1
3	0.0354	2.0	56.5

Experiments with platinum chloride showed that 88 per cent. of activity due to actinium-*D* obtained by recoil on the magnesium foil could be obtained in a precipitate of potassium platinichloride.

It was also shown that the actinium-*D* was precipitated with the thallium from a solution containing sulphuric acid, oxidised by bromine water to which ammonia was added, a reaction analogous to that employed by Metzner for thorium-*D*. It is also completely precipitated with thallium sulphide by ammonium sulphide and with potassium iodide. It is not precipitated as hydroxide or as sulphide from an acid solution.

These experiments show that actinium-*D* cannot be separated from thallium.

#### Summary.

It has been shown (1) that radium-*A* and polonium are chemically similar and non-separable; (2) that thorium-*D* is similar to thallium; (3) that actinium-*B* is not only closely allied to lead but non-separable from it; and (4) that actinium-*D* and thallium are two chemically non-separable substances.

These experiments therefore confirm the correctness of the general theoretical law governing the evolution of the radio-elements through the Periodic Table.

I desire to thank Dr. Giesel and the Chinin Fabrik of Brunswick for their kindness in lending a powerful actinium preparation for this research.

I am indebted also to Mr. F. Soddy, F.R.S., for his continued help and advice, and for the use of materials employed in carrying out this research.

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XCIV.—*The Rotatory Dispersive Power of Organic Compounds. Part I. The Measurement of Rotatory Dispersion.*

By THOMAS MARTIN LOWRY.

ABOUT eight years ago experiments were begun with a view to extend the measurement of optical rotatory power to colours other than the yellow sodium light, which at that time was used almost exclusively in chemical laboratories throughout the world. The importance of this extension was obvious. The form of the rotatory-dispersion curves was in most cases not known, but cases of anomalous dispersion had been detected with considerable frequency amongst the substances which had been used most commonly in polarimetric investigations. It was clear that progress was likely to be slow until it was possible to determine the influence of temperature, solvent, concentration, and chemical constitution upon the whole form of the rotatory-dispersion curve, rather than on one single point, which had been selected solely because light of that particular wave-length was cheaply and easily produced.

The aim of the investigation now described was not merely to make observations in the case of a few selected substances, but rather to establish new methods of measuring rotatory dispersion, which should be so simple and easy as to render them generally available for the ordinary routine measurements of the laboratory.

It soon became evident that such standard methods could only be established after an exhaustive study of all the most promising possibilities, and, moreover, that if the methods were to be of permanent utility they must be capable of giving results of the highest order of accuracy, and must therefore be tested with a stringency far exceeding the requirements of present-day routine. It was with this object in view that experiments were begun on the rotatory dispersion of light in quartz (*Phil. Trans.*, 1912, A, **212**, 261), since there was no other way in which readings of large magnitude could be taken and then reproduced month after month without any perceptible variation. The labour involved in these experiments has been amply justified by a progressive simplification of methods and of apparatus, which has already brought the measurement of rotatory dispersion within the reach of the advanced student as well as of the original investigator. It is proposed in the following pages to describe these simplified methods of measurement and some of the observations and conclusions to which they have led.

## A.—Sources of Light.

In the experiments on quartz it was found that readings which could be reproduced with a variation of only a few parts per million could be taken with light of some 24 wave-lengths in the visible region of the spectrum (*Phil. Trans.*, 1912, A, 212, 288, 389). Many of these were obviously unsuitable for general use, except when a very large number of different wave-lengths are required, for example, to establish the exact form of some anomalous curve. In particular, it was recognised that the spectra of metallic arcs burning between terminals of copper or brass were not likely to be widely used, both because of the relative complexity of the apparatus, and because of the disagreeable flicker which is almost inseparable from such sources of light; but it was not possible to rule out the cadmium lines on this ground, as three of these, namely:

{ The red line.....	wave-length 6438.4722
{ The green line.....	5085.8249
{ The blue " .....	4789.9107

are of unsurpassed spectral purity, and have already been used very largely as principal standards of wave-length. If it were not for the difficulty of producing a powerful cadmium spectrum, these three lines would undoubtedly appear in the forefront in all measurements of rotatory dispersion; even at the present time they cannot safely be set aside, as the enclosed cadmium arc, which is now somewhat of a curiosity, may at any moment become a commercial product capable of being used under ordinary laboratory conditions. In view of these considerations, a large number of measurements were made with a cadmium spectrum produced by burning an arc between poles of a silver-cadmium alloy (*Phil. Mag.*, 1909, [vi], 18, 320). The silver arc-spectrum, although much easier to produce, was used but little; one of the green lines is a doublet, occupying practically the same position as the green mercury line, whilst the beautiful dark green line does not differ from it sufficiently to justify the trouble of taking a second set of "green" readings except in the case of substances showing anomalous rotatory dispersive power. A similar statement may be made about the green thallium line; a powerful and steady light can now be produced with great ease by vaporising the chloride from a silica bulb in a stream of oxygen and passing it into a flame (*P.*, 1912, 28, 65); but it is not likely to be used much, except in laboratories where the arc-spectra are not available.

The accumulated experience of several years has proved conclusively that (at least until the enclosed cadmium arc becomes a commercial proposition) no better line can be selected for standard

polarimetric measurements than the green mercury line of wave-length 5461. By means of the echelon spectroscope, the line can be resolved into eight components (Stansfield, *Phil. Mag.*, 1909, [vi], 18, plate XII); but these extend over a range of less than half an Ångström unit, and are distributed very symmetrically about a dominant doublet, so that the line may be regarded for most purposes as a pure monochromat. Its availability as such for polarimetric work is sufficiently proved by the fact that it has given perfectly clean readings ( $12789.19^\circ$  and  $12789.21^\circ$ ) after passing through half a metre of quartz. It was, indeed, in the testing of quartz that this line was shown to be unique, since in no other case was it possible with certainty to attribute small variations in the readings to causes which were entirely independent of the source of light. The violet line of wave-length 4359 is also of unique value as a source of monochromatic violet light, and as such is likely to remain for many years the second absolutely essential feature in all ordinary measurements of rotatory dispersion. It will be sufficient to point out that where two substances differ in rotatory power by 137 units at wave-length 4359, the dark blue cadmium line of wave-length 4687 gives a difference of only 71 units, whilst the light blue cadmium line of wave-length 4800 gives a difference of only 54 units, the values being assumed to be equal at wave-length 5461. The light blue cadmium line is not easy to read with accuracy even at the present time; the dark blue cadmium line proved to be so difficult and fatiguing that it was soon abandoned as a source of light for routine measurements; the violet mercury line, on the other hand, when derived from a modern commercial mercury arc, is so powerful and steady that it can be read with ease and accuracy, using a half-shadow angle of only  $4^\circ$  to  $5^\circ$ . The presence of two satellites introduces an error which does not exceed 1 part in 10,000, and may therefore be neglected in all readings of less than  $100^\circ$ .

The selection of a suitable line for use at the red end of the spectrum is less easy. The red cadmium line of wave-length 6438 is easier to read than the red zinc line of wave-length 6364; but the red lithium line of wave-length 6708 is the one that has been used most frequently. Even under favourable conditions it can only be read with a half-shadow angle of  $7^\circ$  or  $8^\circ$ , and little reliance can be placed on the second decimal ( $0.01^\circ$ ) of the readings; but these disadvantages are compensated by its greater wave-length, which serves to magnify considerably the effects of rotatory dispersion.

The first routine-measurements were made with a series of nine lines:

Li.	Ca.	Na.	Hg.	Hg.	Ca.	Ca.	Ca.	Hg.
6708	6438	5893	$\left\{ \begin{smallmatrix} 5790 \\ 5769 \end{smallmatrix} \right\}$	5461	5085	4800	4678	4359
Red.		Yellow.		Green.		Blue.		Violet.

The series was soon reduced to eight by omitting the dark blue cadmium line. This would be one of the most valuable of the series if it could be more easily read, but the strain involved was so excessive that it had to be abandoned. The yellow mercury doublet 5790 and 5769 was also dropped as being redundant, and also because it is so far from being monochromatic that there is little real difficulty in reading the components separately. If a powerful cadmium arc were available, the above series (with the mercury doublet omitted, but the dark blue cadmium line restored) would give an almost ideal list of eight monochromatic lines, which might be relied on to survive the test of many years of actual service. It would include some of the purest and most powerful lines that have been observed amongst the spectra of the elements, and would require a minimum amount of apparatus both for producing the spectra and for resolving them into their constituent lines.

Polarimetric measurements with this series of lines soon revealed the fact that most of the curves belonged to one family, so that agreement at two points usually implied agreement throughout the whole of the rotatory-dispersion curves. Under these conditions, when once the form of any particular curve had been established, attention was concentrated on the careful measurement of a smaller number of lines; the cadmium lines, which still involved the use of a rotating metallic arc, were therefore frequently omitted, thus reducing the series to four lines:

Li.	Na.	Hg.	Hg.
6708	5893	5461	4359

(Compare Dorn and Lohmann, *Ann. Physik*, 1909, [iv], 29, 535.)

Finally, when it was discovered that the rotatory-dispersion curves could be expressed by an equation involving only two constants, attention was directed almost exclusively to a very careful reading of the green and violet mercury lines. From these readings the other points on the curve could then be calculated with a degree of accuracy exceeding that which could be attained in any one individual series of observations. The lithium and sodium lines were then no longer an essential part of the scheme of measurements; but it was desirable to retain the red line as a check upon the normal character of the curves, whilst the sodium line was still used sometimes in order to keep directly in touch with earlier observations.



## B.—Apparatus.

From the preceding statement it will be seen that in the course of seven or eight years the measurement of rotatory dispersion has been reduced from tedious and fatiguing observations of eight and nine wave-lengths to the rapid and easy observation of two lines only. An equal simplification has been effected in the apparatus used. At first the light was purified by passing through a constant-deviation spectroscope before entering the polarimeter. The presence of stray light rendered necessary the addition of a direct-vision prism on the eye-piece as employed by Perkin (*T.*, 1906, **89**, 615) for a similar purpose. This twofold spectroscopic purification (*Phil. Trans.*, 1912, *A*, **212**, 268) still provides the most luxurious way of reading a polarimeter with lights of various colours, and is essential in all cases in which a complex spectrum has to be resolved, as, for instance, when the cadmium lines are read with



Simple apparatus for measuring rotatory dispersion.

NOTE.—The apparatus is shown as arranged for reading the magnetic rotatory power of a shortened column (100 mm.) of liquid (compare Part III. of this series of papers).

the help of a cadmium-silver arc. In the case of the red lithium and the violet mercury line, however, the double resolution necessitates a greater sacrifice of light than is practicable in taking readings at the ends of the visible spectrum; these lines must therefore be read with a direct-vision prism only. It is one of the merits of the scheme of standard wave-lengths discussed in the preceding paragraphs that the four lines specially chosen for routine measurements can all be read with this simplified arrangement. With the help of an enclosed arc, it should also be possible to read the cadmium lines in the same way, thus giving a full series of eight lines without the use of an auxiliary spectroscope.

The actual arrangement, as applied to the measurement of magnetic rotatory power, is shown in the diagram, where *A* is a mercury lamp, *B* is a condensing lens, *C* is the triple-field, *D* is a slit, *E* is the analysing prism, *F* is a direct-vision prism attached to the eyepiece. In adapting an ordinary polarimeter for measurements of rotatory dispersion, it is only necessary to add to it the direct-vision prism *F*, and the slit *D*. The latter may be merely two pieces of

paper fixed to the glass window which protects the polarising prisms. Apart from the mercury lamp, the cost of the adaptation is therefore insignificant. If a full field is required it is convenient to use an extra dense direct-vision prism to separate the mercury green line from the yellow doublet, but it is still advisable to use a light prism for the violet, as the denser prisms tend to cut off the light.

The apparatus for producing light need not be described in detail. Several mercury lamps specially suited for spectroscopic and polarimetric work have already been described (*Trans. Faraday Soc.*, 1912, 7, 267; *Proc. Roy. Inst.*, April 18th, 1913; compare *Engineering*, April 24th, 1913). The other methods of illumination are set out in the paper already referred to (*Phil. Trans.*, 1912, A, 212, 269).

Apparatus has also been devised for taking polarimetric readings in the infra-red and ultra-violet regions of the spectrum. This will be described in detail in connexion with experiments on the dispersive power of quartz, of which it formed an essential feature.

The expenses of the experiments described in this series of papers have been defrayed to a very large extent by generous grants from the Government Grant Fund of the Royal Society, for which the author wishes to express his gratitude. He also wishes to thank Mr. W. P. Paddison and Mr. H. R. Courtman for valuable assistance in the experimental work.

#### CXV.—The Rotatory Dispersive Power of Organic Compounds. Part II. The Form of the Rotatory-dispersion Curves.

By THOMAS MARTIN LOWRY and THOMAS WILLIAM DICKSON.

PERHAPS the most interesting result of the investigations now described has been to disclose the fact that the rotatory-dispersion curves of many organic compounds are of such a simple form that they can be expressed by means of equations containing only two arbitrary constants.

In the case of quartz, the rotatory power in the visible region of the spectrum was expressed by the equation:

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k}{\lambda^2},$$

where  $\lambda_1^2 = 0.010627$  represents an absorption band in the inaccessible ultra-violet region at wave-length 1030 ( $0.1030\mu$ ),  $\lambda_2^2 = 78.22$  represents a band in the deep infra-red at wave-length

88,440 (8.844 $\mu$ ), whilst the third term implies the existence of a band so far out in the ultra-violet that  $\lambda_3^2$ , the square of its wave-length, is negligible. In order to make the equation express the rotatory power of quartz in the ultra-violet region, it is necessary to give a finite value to  $\lambda_3^2$ ; the equation then includes a third term,  $\frac{k_s}{\lambda^2 - \lambda_3^2}$ , and involves not less than six constants.

An investigation of the rotatory-dispersive power of a large number of organic compounds has shown that both the optical and the magnetic dispersions can be expressed by the simple equation:

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}.$$

This equation has the merit of separating completely and easily the rotatory power of a substance from its dispersive power, so that these can now be measured and discussed as separate and independent properties.

"*Absolute Rotatory Power.*"—Every substance which obeys this dispersion law may possess a rotatory power ranging from zero to infinity according to the wave-length of the light employed. A casual measurement of its optical rotatory power for one arbitrary wave-length is therefore no guide to its power of rotating the plane of polarisation, and does not afford any real measure of the asymmetry of the molecule. Such a measure is, however, afforded by the constant  $k$  of the above equation; this may be described as the "*rotation constant*" of the equation. From the form of the function in which it appears, it is clear that the "*rotation constant*"  $k$  has not the same dimensions as the "*rotation*"  $\alpha$ , but must represent the product of a rotation multiplied by the square of a length. But it is at once evident that the numerical value of  $k$  will be equal to the numerical value of  $\alpha$  when  $\lambda^2 - \lambda_0^2 = 1$ . This particular value of  $\alpha$  (which, but for the difference in dimensions, might be substituted for  $k$  in the equation) we propose to describe as the "*absolute rotation*," representing it by the symbol  $\alpha_a$  or  $\alpha_{abs}$ . The equation might indeed be rewritten as:

$$\frac{\alpha}{\alpha_0} = \frac{[L]^2}{\lambda^2 - \lambda_0^2},$$

where  $[L]$  is simply the unit of length.

It should be noted that the term "*absolute*" is used here to describe the selection of a particular wave-length as a standard in recording the rotatory power of a substance. It may therefore be applied either to the observed rotation, to the specific rotation, or to the molecular rotation, using for this purpose the symbols:

$$\alpha_{obs}, \quad [\alpha]_{obs}, \quad [M]_{obs}$$

In handling the equation, it is convenient to express the wave-

lengths in microns, so that the sodium doublet has wave-length  $0.5893\mu$ , whilst the corresponding values for the green and violet mercury lines are  $0.5461\mu$  and  $0.4359\mu$ . As  $\lambda_0^2$  is usually small, at least in the case of colourless substances, the "absolute rotatory power" is the value which would be observed at a wave-length, given by  $\lambda^2 = 1 + \lambda_0^2$ , not far removed from 1 micron or 10,000 Angström units. Thus the "absolute rotatory power" of a large number of simple organic compounds for which  $\lambda_0^2 = 0.02$  (approx.) is substantially identical with the values which would be observed if readings were taken with the infra-red mercury line at wave-length  $1.0140\mu$  or 10,140 Angström units; these "absolute rotations" are about 28 per cent. of the values for the green mercury line, and 33 per cent. of the values for the yellow sodium doublet.

"Dispersive Power."—The simplest method of expressing the dispersive power of a substance is to give the ratio  $\alpha_{4359}/\alpha_{5461}$  of the readings for the violet and green lines of the mercury spectrum. This may be described as the chief "*dispersion ratio*" of the substance. But with the help of the formula given above there is no difficulty in providing a measure of the dispersion which shall be independent of the particular wave-lengths selected for observation. Such a measure is afforded by the "*dispersion constant*"  $\lambda_0^2$  of the equation.

This constant represents the square of the wave-length of the dominant absorption band. If the band were so far removed into the extreme ultra-violet that  $\lambda_0^2$  became negligible, the substance could obey Biot's law:  $\alpha = k/\lambda^2$ , the rotation being inversely proportional to the square of the wave-length. Biot's law appears, indeed, to express the lower limit of dispersive power as it would be observed in an absolutely transparent medium. Such a medium does not appear to exist amongst optically active compounds, and if it did its optical rotatory power would probably be reduced to the vanishing point. In all the actual cases that have been studied the dispersion is increased by the presence of absorption in the ultra-violet region, whereby  $\lambda^2$  is converted into  $\lambda^2 - \lambda_0^2$ . The nearer the wave-length  $\lambda_0$  of the absorption band, the greater will be the dispersive power of the medium, at least until the band passes over to the infra-red side of the wave-lengths under consideration. This increase of dispersion depends directly on the magnitude of  $\lambda_0^2$ , which is thus a measure of the dispersive power of the medium as distinct from the dispersion, which seems to be separable from the phenomenon of optical rotation in every medium in which it occurs.

It is remarkable that the dispersion ratio  $\alpha_{4359}/\alpha_{5461}$  never seems to fall much below 1.630, whether in quartz, in water, in a hydro-

carbon, or in simple compounds containing carbon, hydrogen and oxygen, provided that these do not show anomalous rotatory dispersion. In all these substances there seems to be a dominant absorption band between  $\lambda_0^2 = 0.01$  and  $0.02$ . It is therefore convenient to take a substance for which  $\lambda_0^2 = 0.01$  as possessing unit dispersive power, and to measure the "dispersive power" of any other substance by the constant  $100\lambda_0^2$ . On this scale, the "dispersive power" of the simpler alcohols would be about 2.0 units for magnetic rotations, and 2.8 units for optical rotations, whilst the dispersive power of carbon disulphide (magnetic) would be as high as 4.8 units.

*Exact Form of the Curves.*—In view of the small magnitude of the readings, the formula for the rotatory dispersion in organic compounds could not be tested with the same accuracy as in the case of quartz. These readings were taken to six or seven significant figures, but even then it was not possible to detect the influence of more than one of the two known infra-red bands, nor could the position of the second ultra-violet band be determined even approximately from readings in the visible region of the spectrum. When investigating the simpler organic compounds, it was not easy to take readings which could be relied on to 1 part in 1000; that is, one or two hundredths on a reading of  $10^\circ$  to  $20^\circ$ . It was therefore impossible, in the case of substances of normal dispersive power, to determine whether the dispersion was influenced by more than one "free period" of vibration; such a question could only be answered by increasing the magnitude of the observed rotations and by extending the readings as far as possible into the ultra-violet and infra-red regions of the spectrum.

From the practical point of view, however, it is a distinct advantage that these requirements can be set aside by using a simple formula which expresses the form of the curves beyond the limits of accuracy which are possible in ordinary observations. Even in the case of quartz, if the dispersion ratios are taken out to three places of decimals instead of six, no errors greater than 0.001 are introduced when the figures are calculated with the help of the simple formula now put forward for organic compounds.

*Numerical Data.*—In establishing the form of the rotatory dispersion curve for the simpler organic compounds, it was impossible to come to any satisfactory conclusion on the basis of a few readings taken with a small number of selected substances. Even in reading the sodium and mercury (violet) lines, it is easy to make an error of, say,  $0.02^\circ$  in the observations and 0.002 in the dispersion ratios, whilst in the case of the lithium and cadmium lines the errors may easily be twice as great. For this reason great

importance attaches to the cumulative evidence afforded by the data collected together in table I. Each figure in this table represents an average figure obtained from some 20 to 100 settings of the instrument, so that the number of observations condensed into a single table can scarcely be less than 20,000. The value of this accumulation of data is at once seen in the third panel of the table, which contains data for 17 alcohols, 6 acids, and 2 paraffins. When the dispersion ratios for these 25 substances are averaged, the agreement with the calculated figures is practically perfect, but the individual values are seen to vary by  $\pm 0.003$  in the case of the yellow sodium and green cadmium readings, by  $\pm 0.005$  for lithium red,  $\pm 0.008$  for cadmium red, and  $\pm 0.01$  for cadmium blue. No significance attaches to variations in the violet to green ratio (which is probably subject to an error of  $\pm 0.002$ ), as this was merely used to decide which substances should be included in each of the different panels.

The substances included in the lower panels of the table are not only more dispersive than those in the earlier panels, but also have much higher rotatory powers. Their dispersion ratios are therefore much more accurate, and show an extremely satisfactory agreement with the calculated ratios in spite of the relatively small number of readings which are included in each average.

*Magnetic and Optical Rotatory Dispersion.*—It is not proposed to discuss at this point the validity of Wiedemann's law of the proportionality of optical and magnetic rotatory power throughout the spectrum, but attention may be directed to the proof that is now afforded of the identical form of the two types of dispersion curves. Most of the data in the table are for magnetic rotatory dispersion, but identical formulæ have served for the calculation of optical rotatory dispersion. This is seen most clearly by the identical values, shown in the first panel of the table, for the "optical" and "magnetic" dispersion ratios for quartz. The statement is also true of substances which do not obey Wiedemann's law. In particular, it may be noted that the dispersion ratios for phenylthylcarbinol (opt.), shown in column 6, agree very closely with those for allyl alcohol (mag.), as well as with those calculated from the formula. The magnetic values for this carbinol, on the other hand, are found in column 8, in close agreement with the ratios for the optical and magnetic rotatory dispersions in phenylmethylcarbinol.

*Graphic Representation.*—When the rotatory power of a substance is plotted against the square of the wave-length, the dispersion curve (if normal) is a simple rectangular hyperbola running asymptotically to zero rotatory power at infinite wave-length and to infinite

Form of the Rotatory-dispersion Curve.

		Red.		Green.			Blue.		Violet.
		Li	Ca	Hg	Cd	Hg	Cd	Cd	
1. Quartz (magnetic)	Quartz (optical)	6708	6438	5893	5461	5086	4800	4573	Hg 4359.
		0.816	0.706	0.851	1.167	1.000	1.318	—	1.627
		0.818	0.706	0.851	1.164	1.000	1.319	1.394	1.627
2. Methyl alcohol (mag.)	Calculated $\epsilon_m = 0.2809 \lambda_0^{-2} - 0.0173$	0.619	0.707	0.851	1.164	1.000	1.318	1.394	1.627
	Ethyl "	0.645	0.707	0.851	1.164	1.000	1.315	1.386	1.624
	Propyl "	0.638	0.708	0.849	1.166	1.000	1.318	1.393	1.625
3. <i>tert</i> -Propyl alcohol (mag.)	Calculated $\epsilon_m = 0.2509 \lambda_0^{-2} - 0.0173$	0.642	0.709	0.850	1.161	1.000	1.315	1.390	1.625
	Average	0.649	0.707	0.851	1.164	1.000	1.318	1.393	1.626
	Calculated $\epsilon_m = 0.2509 \lambda_0^{-2} - 0.0173$	0.642	0.702	0.850	1.163	1.000	1.320	—	1.634
Average for 17 alcohols	<i>n</i> -Butyl	0.649	0.707	0.849	1.163	1.000	1.328	—	1.637
	<i>sec</i> -Butyl	0.648	0.707	0.849	1.162	1.000	1.321	—	1.635
	<i>tert</i> -Butyl	0.645	0.713	0.846	1.164	1.000	1.320	1.391	1.631
	<i>sec</i> -Amyl	0.650	0.702	0.852	1.169	1.000	1.325	—	1.634
	<i>tert</i> -Amyl	0.647	—	0.850	1.160	1.000	—	—	1.631
	<i>sec</i> -Hexyl	0.651	0.705	0.852	1.165	1.000	1.321	—	1.636
	<i>tert</i> -Hexyl	0.647	0.708	0.855	1.162	1.000	1.320	—	1.635
	<i>sec</i> -Heptyl	0.648	—	0.849	1.163	1.000	—	—	1.633
	<i>tert</i> -Heptyl	0.647	0.705	0.851	1.166	1.000	1.320	1.394	1.635
	<i>sec</i> -Octyl	0.642	0.705	0.849	1.163	1.000	1.322	—	1.634
	<i>tert</i> -Octyl	0.644	0.703	0.853	1.165	1.000	—	—	1.635
	<i>sec</i> -Nonyl	0.642	—	0.848	—	1.000	—	—	1.634
	<i>tert</i> -Nonyl	0.645	—	0.849	—	1.000	—	—	1.634
	<i>sec</i> -Decyl	0.644	—	0.849	—	1.000	—	—	1.634
	<i>tert</i> -Decyl	0.646	0.708	0.850	1.165	1.000	1.322	—	1.636
	<i>sec</i> -Undecyl	0.646	—	0.849	—	1.000	—	—	1.634
	<i>tert</i> -Undecyl	0.646	—	0.849	—	1.000	—	—	1.634
	<i>sec</i> -Dodecyl	0.646	—	0.849	—	1.000	—	—	1.634





Form of the Rotatory-dispersion Curve (continued).

		Yellow.			Green.			Blue.		Violet.
		Li	Ca	Na	Hg	Cd	Cd	Cd	Hg	
5. <i>sec.</i> -Amyl alcohol (opt.)	$\text{CH}_3\text{CH(OH)C}_5\text{H}_{11}$	0.608	0.638	0.893	0.961	1.000	1.000	1.000	1.000	1.000
	$\text{CH}_3\text{CH(OH)C}_6\text{H}_{13}$	0.642	—	0.846	1.000	1.169	—	—	—	1.652
	$\text{CH}_3\text{CH(OH)C}_7\text{H}_{15}$	0.638	—	0.847	1.000	—	1.331	—	—	1.653
	$\text{CH}_3\text{CH(OH)C}_8\text{H}_{17}$	0.640	0.699	0.847	1.000	1.168	—	1.407	—	1.648
	$\text{CH}_3\text{CH(OH)C}_9\text{H}_{19}$	0.637	—	0.846	1.000	—	—	—	—	1.653
	$\text{CH}_3\text{CH(OH)C}_{10}\text{H}_{21}$	0.641	—	0.848	1.000	—	—	—	—	1.651
	$\text{CH}_3\text{CH(OH)C}_{11}\text{H}_{23}$	0.643	—	0.850	1.000	—	—	—	—	1.651
	$\text{CH}_3\text{CH(OH)C}_{12}\text{H}_{25}$	0.645	—	0.848	1.000	—	—	—	—	1.653
	Average	0.641	—	0.847	1.000	—	—	—	—	1.651
	Calculated $\alpha_D = 0.2745 \lambda_D^2 + 0.0237$	0.644	0.702	0.848	1.000	1.163	1.329	1.406	1.651	—
6. Allyl alcohol (mag.)	$\text{C}_3\text{H}_5\text{OH}$	0.641	0.700	0.847	1.000	1.177	1.332	—	—	1.672
	Phenylalcohol (opt.)	0.637	0.700	0.845	1.000	1.174	1.339	1.421	1.674	—
	Calculated $\alpha_D = 0.2658 \lambda_D^2 + 0.0293$	0.639	0.695	0.846	1.000	1.173	1.337	1.418	1.673	—
7. <i>iso</i> -Valeric acid (opt.)		0.631	0.685	0.831	1.000	1.178	1.355	—	—	1.710
	Calculated $\alpha_D = 0.2607 \lambda_D^2 + 0.0375$	0.632	0.6915	0.832	1.000	1.179	1.352	—	—	1.710
8. Phenylalcohol (mag.)	$\text{C}_6\text{H}_5\text{CH(OH)C}_2\text{H}_5$	0.634	0.689	0.835	1.000	1.181	1.362	1.451	1.731	—
	$\text{C}_6\text{H}_5\text{CH(OH)C}_3\text{H}_7$	0.629	0.687	0.833	1.000	1.184	1.361	—	—	1.736
	$\text{C}_6\text{H}_5\text{CH(OH)C}_4\text{H}_9$	0.624	0.685	0.833	1.000	1.184	1.363	—	—	1.739
	Average	0.629	0.687	0.838	1.000	1.183	1.362	—	—	1.735
9. Carbon disulphide (mag.)		0.627	0.687	0.839	1.000	1.183	1.362	1.450	1.736	—
	Calculated $\alpha_D = 0.2553 \lambda_D^2 + 0.0429$	0.624	0.686	0.835	1.000	1.180	1.376	1.464	1.764	—
	Calculated $\alpha_D = 0.2469 \lambda_D^2 + 0.0483$	0.622	0.682	0.836	1.000	1.186	1.3726	1.466	1.764	—

rotatory power at a wave-length  $\lambda_0$  corresponding with the natural period of free vibration in the molecule.

A very simple method of testing the form of the dispersion curve is to plot the reciprocals of the rotatory powers (or of the dispersion ratios) against the squares of the wave-lengths, using for this purpose the following data:

Li 6708	Cd 6438	Na 5893	Hg 5461	Cd 5086	Cd 4800	Cd 4678	Hg 4359
$\lambda^2=0.45$	0.4145	0.3473	0.2982	0.2587	0.2301	0.2189	0.1900

If the simple dispersion formula is valid, the observations will then plot out to a straight line. An accurate straight line would only be obtained if the dispersion obeyed the simple law:  $\alpha = k/(\lambda^2 - \lambda_0^2)$ . If two terms were required to express the dispersion, as in the case of ethyl tartrate and other "anomalous" substances, thus:

$$\alpha = k_0/(\lambda^2 - \lambda_0^2) \pm k/(\lambda^2 - \lambda_1^2),$$

the reciprocals would no longer plot out to a straight line. The accuracy of the observations would not, however, usually be sufficient to detect the presence of a second term of similar sign unless there were a considerable difference in the magnitude of the two "dispersion-constants."

### Summary and Conclusions.

(1) The rotatory dispersion of a large number of simple organic compounds may be expressed by the formula:

$$\alpha = k/(\lambda^2 - \lambda_0^2),$$

where  $k$  is the "rotation constant" and  $\lambda_0^2$  is the "dispersion constant" of the substance.

(2) The "rotation constant"  $k$  is numerically equal to the "absolute rotatory power,"  $\alpha_0$ , which represents the rotatory power of the substance for a wave-length  $\lambda$ , such that  $\lambda^2 - \lambda_0^2 = 1$ . Measuring  $\lambda$  in microns, this wave-length is a little greater than  $1\mu$ , or 10,000 Ångström units.

(3) The "dispersive power" of a substance is conveniently measured by a unit which is numerically equal to  $100\lambda_0^2$ . The magnetic dispersive power of the simpler alcohols is about 2.0 of these units, whilst that of carbon disulphide is 4.8 units.

(4) The formula can be applied both to magnetic and to natural rotatory powers.

(5) The rotatory-dispersion curves for normal substances may be plotted out as simple rectangular hyperbole against the square of the wave-length, or appear as straight lines if the reciprocals of the rotatory powers are plotted.

CXVI.—*Perezone*.

By FREDERIC GEORGE PERCY REMFRY.

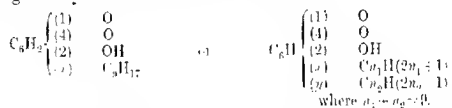
PEREZONE (pipitzahoic acid) is a crystalline compound occurring in relatively large quantities in the root, "Raiz del Pipitzahuac," of a plant, *Perezia ednata*, found in Mexico. It was first examined by Weld (*Annalen*, 1885, **95**, 188), and has since been the subject of extended investigations by Anschütz and Leather (*Ber.*, 1885, **18**, 709, 715; 1886, **49**, 709) and Mylius (*Ber.*, 1885, **18**, 936), whose more important results may be summarised as follows.

Perezone has the empirical formula  $C_{15}H_{15}O_3$ , forming salts,  $C_{15}H_{15}O_3M$ , due to the presence of a phenolic group. It has also the properties of a quinone, in that it (1) possesses a deep orange colour, (2) is readily reduced to a colourless substance, which is quickly reoxidised spontaneously in the air, and (3) yields with aniline and other amines, amino-derivatives, such as anilino-perezone,  $C_{15}H_{15}O_3(NHPh)$ , which are hydrolysed by boiling with dilute acids, yielding hydroxyperezone,  $C_{15}H_{15}O_4$ . The latter substance is dehydrated by concentrated sulphuric acid, yielding perezinone,  $C_{15}H_{13}O_3$ , which has both quinonoid and phenolic properties.

Perezone contains an unsaturated linking, for it yields an unstable dibromide.

Attempts to obtain definite compounds from it by reduction, the action of sulphuric acid, phenylhydrazine, or hydroxylamine, or by distillation with zinc dust, as also an attempt to prepare its ethyl ether, were unsuccessful, but an acetyl derivative, to which reference will be made later, was obtained.

The general behaviour of perezone, and particularly its similarity to hydroxythymoquinone, led Anschütz to suggest that it is a hydroxybenzoquinone, containing not more than two substituent alkyl groups, of which one is unsaturated, and he proposed the following embryonic constitutional formulæ:



No further investigations of this acid appear to have been carried out until 1906, when Sanders (*P.*, **22**, 134) briefly recorded the results of a number of experiments with it. Sanders rejects the established formula, and proposes in its place  $C_{10}H_{11}O_2$ , but the reasons for this change are not given. He also states that "by prolonged heating above its melting point it loses carbon monoxide and carbon dioxide, giving at first a lemon-yellow sublimate, which melts at 58–59°, and finally a beautifully crystalline, colourless

sublimate, which is insoluble in water, but soluble in most organic solvents. This compound,  $C_{11}H_{14}O_2$ , crystallises from acetone or benzene in glistening prisms, melting at  $140^\circ$ , and having an odour of camphor. Its solutions are optically active, a 2 per cent. solution in alcohol having  $[\alpha]_D^{25}$  77.9 at  $25^\circ$ ; it does not react with hydroxylamine or aniline, but with acetic anhydride forms a compound,  $C_{11}H_{14}O_{10}$ , which crystallises from acetone in square plates, melting at  $114-115^\circ$ ."

He further states that perezone is optically inactive, does not contain methoxy-groups, and yields, on fusion with potassium hydroxide, methylhexylene and butyric acid. He states that perezone seems to behave as a hydroxy-ketone.

Perezone had not been the object of any later communication than Sanders's paper (*loc. cit.*) at the time when this work was carried out, and since it exerts very marked physiological action, having purgative properties for which it is much used in Mexico, it was deemed of interest to examine it carefully in order to contribute further to the knowledge of its constitution. Owing to circumstances, it has not been possible to complete the work, and as it is improbable that the author will again be able to take up this problem, the results so far obtained are given in the hope that they may be of assistance to any future investigator.\*

In the first place, it was deemed of importance to establish the empirical formula of perezone by molecular-weight determinations, for Sanders's formula,  $C_{10}H_{14}O_2$ , appeared to be highly improbable in view of the fact that the salts analysed by Weld and Anschütz and Leather were derived from the formula  $C_{15}H_{20}O_3$  by the replacement of one hydrogen atom by a monobasic metal. This was accordingly carried out both by the cryoscopic and ebullioscopic methods, and gave results in agreement with the formula  $C_{15}H_{20}O_3$ . An ultimate analysis confirmed this formula. Sanders's formula for perezone is therefore incorrect.

It next seemed of interest to reinvestigate Sanders's colourless sublimate,  $C_{11}H_{14}O_2$ , melting at  $140^\circ$ , and the compound,  $C_{11}H_{30}O_{10}$ , melting at  $114-115^\circ$ , which he obtained by the action of acetic anhydride on this sublimate. The action of heat on perezone was therefore studied, and it was found that when this compound is heated to  $210^\circ$  an exothermic reaction takes place, the temperature rising to about  $270^\circ$ , and carbon dioxide, water vapour, and an inflammable gas being evolved. The residue, which forms a

\*At the present work had been written up and shortly before its communication (P. 1914, 29, 72). Fichter, Jetzer, and Loepin published an investigation (*Ann.*, 1913, 395, 15) of the properties of hydroxyperezone from the results of which they deduced the constitution of this substance, and of perezone itself. This work covers entirely different ground from the present paper, and is discussed in an addendum.

reddish-black varnish when dissolved in a little alcohol or ether, deposits the compound melting at  $140-141^{\circ}$  (corr.) in well-formed crystals. This compound may also be obtained by sublimation, or by quick distillation of perezone under normal pressure. When pure it is perfectly colourless, and magnificently crystalline. It contains a phenolic hydroxyl group, and may conveniently be designated pipitzol. Analyses and molecular-weight determinations show that it has the formula  $C_{15}H_{20}O_3$ , and is therefore isomeric with perezone. It is optically active, as stated by Sanders, but his figure  $[\alpha]_D 77.9^{\circ}$  was not confirmed, the constant value  $+13.1^{\circ}$  being obtained for the pure substance. It does not react with aniline, hydroxylamine, or phenylhydrazine, and does not decolorise bromine in chloroform solution. When treated with an ethereal solution of magnesium methyl iodide, it gave a compound,  $C_{15}H_{24}O_3$ , melting at  $145^{\circ}$ , which may be termed *tetrahydropipitzol*.

Pipitzol is readily acetylated by means of acetic anhydride, yielding a monoacetyl derivative, *acetylpipitzol*,  $C_{15}H_{18}O_3 \cdot CO \cdot CH_3$ , melting at  $114-115^{\circ}$  (corr.). This is obviously identical with Sanders's compound,  $C_{11}H_{20}O_{10}$ , of the same melting point. Acetylpipitzol is also identical with the product obtained by Anschütz and Leather (*loc. cit.*) by the action of acetic anhydride on perezone under pressure at  $100^{\circ}$ .

When acetylpipitzol is hydrolysed by means of acid, pipitzol is regenerated, but when sodium hydroxide is used, the product is an oil which could not be caused to crystallise.

It is shown that pipitzol is identical with the colourless, crystalline compound, melting at  $141^{\circ}$ , which Anschütz and Leather obtained by the action of ethyl bromide on the silver salt of perezone in an endeavour to form the ethyl ester.

One of the three oxygen atoms in pipitzol is phenolic, the other two appear to be neither hydroxylic, since the compound yields only a monoacetyl derivative, nor quinonoid, since it is colourless, nor ketonic, since it does not react with hydroxylamine, phenylhydrazine, or (in so far as the oxygen atoms are concerned) with magnesium methyl iodide. No definite products were obtained by the oxidation of pipitzol.

Further evidence that perezone is a quinone has been obtained by the action of magnesium alkyl iodides, when *alkylquinones* of this compound were produced.

By-products produced in the preparation of hydroxyperezone and perezinone have also been studied, and, in conclusion, a number of unsuccessful miscellaneous experiments designed to prepare from perezone compounds likely to assist in the elucidation of its constitution are briefly recorded.

## EXPERIMENTAL.

*Perezone.*

The compound used for this investigation was in the form of orange-golden leaflets, which softened at  $102^{\circ}$  and melted at  $103\text{--}105^{\circ}$  (corr.). Further crystallisation from water or alcohol did not alter the melting point.

The figures obtained on analysis were in accordance with those of previous investigators. (Found,  $C=72.7$ ;  $H=8.0$ .  $C_{15}H_{20}O_3$  requires  $C=72.6$ ;  $H=8.0$  per cent.)

Determinations of the molecular weight were carried out by the cryoscopic method in benzene solution:

0.2834 in  $14.8$  gave  $\Delta t = -0.403^{\circ}$ , whence M.W. = 238.

0.2629 „  $14.82$  „  $\Delta t = -0.352^{\circ}$ , whence M.W. = 252.

$C_{15}H_{20}O_3$  requires M.W. = 248.

*Pipitzol*,  $C_{15}H_{20}O_3$ .

This substance is produced in yields varying usually between 25 and 50 per cent. when perezone is heated under different conditions.

When 1 gram of perezone is melted in a small test-tube containing a thermometer, and slowly heated, evident reaction ensues when the temperature reaches  $200\text{--}210^{\circ}$ , for after the source of heat is removed the temperature rises to about  $270^{\circ}$ , whilst the liquid darkens in colour, and appears to boil owing to the escape of a mixture of carbon dioxide, an inflammable gas, and water vapour. When the product is cooled and dissolved in a little ether or alcohol, pipitzol crystallises out.

Pipitzol may also be prepared by the quick distillation of perezone; only a small proportion of the substance distils over at a very high temperature as a very viscous, somewhat coloured oil, which crystallises when treated with solvents, the residue in the distillation flask forming a dark amorphous mass.

It may also be prepared by sublimation, as stated by Sanders (*loc. cit.*).

Ten grams of perezone were heated in a glass dish, into which there was fitted a filter funnel, through the neck of which a thermometer was placed, for one and a-half to two hours at  $160\text{--}170^{\circ}$ . Large fern-shaped crystals formed on the sides of the dish and funnel, and were always more or less coloured, since some of the perezone sublimed unchanged. The crystals were collected, washed with a little cold light petroleum, and recrystallised, first from this solvent, then from alcohol, when pure pipitzol was obtained.

No individual substance corresponding with Sanders's yellow sublimate, melting at 88–89°, was observed, but a part of the sublimed substance which melted at about that temperature was found to be a mixture of perezone and pipitzol. The dark residue left in the dish after the sublimation gave a further quantity of pipitzol when subjected to a distillation with steam.

*Pipitzol* crystallises from alcohol in large, colourless plates, which melt at 140–141° (corr.):

0.1013 gave 0.2706 CO<sub>2</sub> and 0.0738 H<sub>2</sub>O. C=72.8; H=8.1.

C<sub>15</sub>H<sub>20</sub>O<sub>3</sub> requires C=72.6; H=8.0 per cent.

A determination of the molecular weight by the cryoscopic method in benzene gave the following result:

0.2727 in 15.65 gave  $\Delta t = 0.358$ , whence M.W. = 244.

C<sub>15</sub>H<sub>20</sub>O<sub>3</sub> requires M.W. = 248.

The specific rotation was determined in chloroform solution, with the following result:

$\alpha_D + 1.25^\circ$ ;  $c = 4.770$ ;  $l = 2\text{-dm.}$ ;  $[\alpha]_D + 13.1^\circ$ .

This rotation was not altered by further crystallisation of pipitzol from alcohol. In view of the figures given by Sanders, 77.9° for a 2 per cent. solution in alcohol, the rotation of the pure compound was determined under these conditions, when the result was found to agree with that obtained in chloroform solution:

$\alpha_D + 0.58^\circ$ ;  $c = 2.169$ ;  $l = 2\text{-dm.}$ ;  $[\alpha]_D + 13.4^\circ$ .

Pipitzol is slowly volatile with steam. It is fairly readily soluble in cold alcohol, ether, benzene, or acetone, readily so in cold ethyl acetate, or chloroform, and very readily soluble in these solvents when hot. It is sparingly soluble in cold, but fairly readily so in hot, light petroleum. It is insoluble in cold water or aqueous sodium carbonate, but is readily soluble in aqueous sodium hydroxide, yielding a colourless solution, from which it is precipitated unchanged on the addition of acids or on saturating with carbonic acid. A dilute alcoholic solution gives, with a drop of ferric chloride solution, a violet coloration, changing to greenish-black. It does not decolorise bromine in chloroform solution, and does not react with aniline, hydroxylamine, or phenylhydrazine.

*Acetylpipitzol*, C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>·CO·CH<sub>3</sub>.

Acetylpipitzol is readily prepared in almost quantitative yield by boiling pipitzol with acetic anhydride and sodium acetate. The product is poured into water, and basified with sodium carbonate, when acetylpipitzol separates as a crystalline powder. It is washed with water, and recrystallised from light petroleum.

Acetylpipitzol crystallises from light petroleum in large, colourless prisms, which melt at 114–115° (corr.):

0.1546 gave 0.3990  $\text{CO}_2$  and 0.1064  $\text{H}_2\text{O}$ .  $\text{C}=70.4$ ;  $\text{H}=7.6$ .

$\text{C}_{17}\text{H}_{22}\text{O}_4$  requires  $\text{C}=70.3$ ;  $\text{H}=7.6$  per cent.

The molecular weight was determined by the cryoscopic method in benzene solution:

0.1582 in 15.18 gave  $\Delta t = 0.177^\circ$ , whence  $\text{M.W.}=274$ .

$\text{C}_{17}\text{H}_{22}\text{O}_4$  requires  $\text{M.W.}=290$ .

The number of acetyl groups was determined by A. G. Perkin's method (T., 1905, **87**, 109):

0.4779 gave 0.0954  $\text{C}_2\text{H}_4\text{O}_2$ .  $\text{C}_2\text{H}_4\text{O}_2=20.0$ .

$\text{C}_{17}\text{H}_{22}\text{O}_4$  requires for one acetyl group  $\text{C}_2\text{H}_4\text{O}_2=20.7$  per cent.

From the mother liquors of the acid hydrolysis carried out in this manner, pure pipitzol was recovered in practically quantitative yield. The specific rotatory power of acetylpipitzol was determined in chloroform solution:

$\alpha_D 0.96^\circ$ ;  $c=7.782$ ;  $l=2\text{-cm.}$ ;  $[\alpha]_D +6.2^\circ$ .

Acetylpipitzol is insoluble in water, or aqueous sodium hydroxide, and gives no colour with ferric chloride, from which it is clear that pipitzol contains only one phenolic hydroxyl group. Acetylpipitzol is readily soluble in the usual organic solvents, with the exception of light petroleum.

#### *Benzoylpipitzol, $\text{C}_{15}\text{H}_{19}\text{O}_3\cdot\text{COPh}$ .*

This compound was prepared by the Schotten-Baumann method. It forms colourless prisms from light petroleum, melting at  $154\text{--}155^\circ$  (corr.):

0.1508 gave 0.4131  $\text{CO}_2$  and 0.0952  $\text{H}_2\text{O}$ .  $\text{C}=74.7$ ;  $\text{H}=7.0$ .

$\text{C}_{22}\text{H}_{21}\text{O}_4$  requires  $\text{C}=75.0$ ;  $\text{H}=6.8$  per cent.

#### *Identity of Acetylpipitzol with Anschütz and Leather's Product of Acetic Anhydride on Perezone.*

Anschütz and Leather (*loc. cit.*) attempted to prepare an acetyl derivative of perezone by heating the acid in a sealed tube with acetic anhydride for three days at  $100^\circ$ . In this way they obtained a colourless, crystalline product, melting at  $115^\circ$ , from which, however, they were unable to regenerate perezone by the action of potassium hydroxide. This fact, coupled with the circumstance that the compound was colourless—although an acetyl derivative of a hydroxyquinone should be coloured—caused them to doubt that they had obtained a true acetyl derivative of perezone, in spite of the fact that analyses of the compound agreed well for monoacetyl-perezone.

A quantity of the above substance was prepared by the method given by these authors, and was obtained in colourless plates and prisms from light petroleum, which melted at  $114\text{--}115^\circ$  (corr.). It



was insoluble in alkalis, and gave no colour with ferric chloride or Millon's reagent for phenols, and was therefore completely acetylated. The melting point was identical with that of acetyl-pipitzol, and a mixture of the two melted at the same temperature as the two substances separately. Their properties are similar, and the figures given on analysis agree with those required by the formula  $C_{15}H_{19}O_5 \cdot CO \cdot CH_3$ . A determination of the acetyl groups showed that only one was present, as with acetyl-pipitzol, and the product of hydrolysis left in the liquors proved identical with pipitzol, melting at  $140^\circ$ , and not depressing the melting point of the latter. An analysis of the hydrolytic product also gave results agreeing with those required from pipitzol. (Found,  $C=72.3$ ;  $H=8.3$ .  $C_{15}H_{19}O_5$  requires  $C=72.6$ ;  $H=8.0$  per cent.)

Thus the effect of acetic anhydride under pressure on perezone is primarily the same as that of heat, apparently bringing about some rearrangement of the atoms within the molecule. Attempts have been made by the present author to obtain a true acetyl derivative of perezone by heating with acetic anhydride and fused sodium acetate and acetyl chloride under ordinary pressure, but without result, no change apparently taking place.

*Identity of Pipitzol with Anschütz and Leather's Product of the Action of Ethyl Bromide on the Silver Derivative of Perezone.*

Anschütz and Leather (*loc. cit.*) also attempted to make the ethyl ether of perezone by heating the silver compound under pressure for one hour at  $100^\circ$  with ethyl bromide, and succeeded in obtaining a very small amount of a colourless, crystalline substance, melting at  $141^\circ$ . As the compound was without colour, they expressed great doubt that it was the required ether, and the amount obtained being insufficient for an analysis or any characterisation, they were unable to examine its properties in any way. The fact that this substance was colourless and melted at  $141^\circ$  at once suggested that it might be identical with pipitzol, which has already been shown to be formed by the effect of heat on perezone. Accordingly, 25 grams of the silver salt were heated in a sealed tube for an hour at  $100^\circ$  with 12 grams of ethyl bromide, and after filtering from the silver bromide, a good yield of a colourless, crystalline substance was easily obtained. This was washed with cold light petroleum and crystallised from the same solvent, when it was obtained in colourless prisms, melting at  $140^\circ$ . A mixture with pipitzol melted at the same temperature, and the two specimens possessed identical properties, such as solubility in potassium hydroxide, insolubility in sodium carbonate, violet colour turning to green with ferric chloride, etc. There was therefore no doubt that the compound obtained by Anschütz and Leather was really pipitzol. The effect of the higher

pressure employed is very noticeable in the time taken to produce the change, three days' heating being required to remove the last traces of perezone when acetic anhydride is used.

*Action of Magnesium Methyl Iodide on Pipitzol.*

The action of magnesium methyl iodide on pipitzol in ethereal solution gave rise to a substance crystallising from dilute alcohol in colourless, prismatic needles, which melted at  $145^{\circ}$ . A mixture with pipitzol melted at about  $115^{\circ}$ :

0.0626 gave 0.1640  $\text{CO}_2$  and 0.0530  $\text{H}_2\text{O}$ .  $\text{C} = 71.4$ ;  $\text{H} = 9.4$ .

$\text{C}_{13}\text{H}_{24}\text{O}_3$  requires  $\text{C} = 71.4$ ;  $\text{H} = 9.5$  per cent.

This substance, *tetrahydropipitzol*, retains the phenolic character of phenol, gives a bright green colour with ferric chloride, and does not decolorise bromine.

*Action of Magnesium Alkyl Iodides on Perezone.*

It has been shown by Bamberger (*Ber.*, 1903, 36, 1625) that when quinones of the benzoquinone type are subjected to the action of magnesium methyl iodide in ethereal solution, the reaction proceeds in part as follows:



Other products of the reaction are quinols and different phenols. In the case of *p*-benzoquinone itself, no additive product was formed, and the author has found that quinol is almost the sole product of the reaction, and is formed in good yield. In order to add further evidence for the quinonoid structure of perezone, it was decided to try the action of magnesium alkyl haloids on it, and the results obtained prove that products similar to those observed by Bamberger were formed.

In the following experiments three molecules of magnesium alkyl iodide were used for each molecule of perezone. A vigorous reaction took place on dropping in the ethereal solution of the acid, and a black mass separated out. The reaction mixture was poured into ice water, and the violet-coloured solution acidified with acetic acid, extracted with ether, and the ether well washed with water.

*Methylquinole of Perezone.*—Clusters of fine, colourless needles from xylene, melting at  $111$ — $112^{\circ}$ :

0.1497 gave 0.3982  $\text{CO}_2$  and 0.1234  $\text{H}_2\text{O}$ .  $\text{C} = 72.5$ ;  $\text{H} = 9.1$ .

$\text{C}_{16}\text{H}_{24}\text{O}_3$  requires  $\text{C} = 72.7$ ;  $\text{H} = 9.1$  per cent.

*Ethylquinole of Perezone.*—Clusters of colourless needles from a mixture of benzene and light petroleum. Melting point  $101$ — $102^{\circ}$ :

0.0801 gave 0.2143  $\text{CO}_2$  and 0.0670  $\text{H}_2\text{O}$ .  $\text{C}=73.0$ ;  $\text{H}=9.0$ .

$\text{C}_{17}\text{H}_{26}\text{O}_3$  requires  $\text{C}=73.4$ ;  $\text{H}=9.3$  per cent.

*Propylquinole of Perezone*.—A clear amber oil, which could not be obtained crystalline; it boils undecomposed at  $245\text{--}250^\circ$ ; 30 mm.:

0.1087 gave 0.2976  $\text{CO}_2$  and 0.0926  $\text{H}_2\text{O}$ .  $\text{C}=74.5$ ;  $\text{H}=9.4$ .

$\text{C}_{18}\text{H}_{28}\text{O}_3$  requires  $\text{C}=74.0$ ;  $\text{H}=9.6$  per cent.

The general properties of the three compounds are the same, and can be described together. They are readily soluble in dilute alkali hydroxides, at first without colour, but the solution quickly becomes brown, and then violet, a characteristic colour reaction given by this class of substances (Bamberger, *Ber.*, 1900, **33**, 3653). They are colourless, and therefore have not the true quinone formula, and are readily oxidised by ferric chloride, giving a quinone-like odour and a bright yellow-coloured compound. In the case of the ethyl compound, a crystalline substance was isolated, which melted at  $96\text{--}97^\circ$ , but not in sufficient quantity for analysis. It gave a purple colour with sodium hydroxide similar to that given by perezone, was easily reduced by zinc dust and acetic acid in the cold, and was oxidised again on keeping in the air. This oxidation product was doubtless formed as follows (compare Bamberger, *loc. cit.*):



When warmed with Millon's reagent, these quinole compounds give a yellow coloration indicating a dihydric phenol—a very useful reaction even when the substance is coloured as are perezone derivatives (Mylus, *Ber.*, 1885, **18**, 946).

#### *Hydroxyperezone and its By-products.*

In the preparation of hydroxyperezone,  $\text{C}_{15}\text{H}_{20}\text{O}_4$ , by the action of sulphuric acid on anilinoperezone, both Anschütz and Leather and Mylius noticed the formation of substances which rendered the purification of the main product somewhat difficult.

The melting point of hydroxyperezone is given as  $134^\circ$  by Mylius, and  $138^\circ$  by Anschütz and Leather, but both gave analyses at least 0.5 per cent. too low in carbon content. Hydroxyperezone has now been obtained in a pure state. It melts at  $138\text{--}139^\circ$  (corr.), and gives the correct figures on analysis (Found,  $\text{C}=68.2$ ;  $\text{H}=7.4$ .  $\text{C}_{15}\text{H}_{20}\text{O}_4$  requires  $\text{C}=68.2$ ;  $\text{H}=7.6$  per cent.). Two by-products have been isolated in the course of its preparation; one is a

substance,  $C_{15}H_{16}O_4$ , melting at  $166-167^\circ$  (corr.), the other a substance which does not melt at  $300^\circ$ , and of which the empirical formula has not been adduced with certainty.

Mylius obtained a compound, melting at  $165-168^\circ$ , as a by-product in the preparation of hydroxyperezone, but it contained chlorine owing to the use of hydrochloric acid in the reaction, and is therefore not identical with the substance mentioned above.

The by-product of hydroxyperezone which does not melt at  $300^\circ$  appears to be identical with an impurity of this substance encountered by Anschütz and Leather in quantities too small to permit of analysis or characterisation. They state only that it did not melt, but decomposed at a high temperature, was fairly readily soluble in alcohol or acetic acid, but almost insoluble in ether or benzene.

Substance,  $C_{15}H_{16}O_3$ , m. p.  $166-167^\circ$  (corr.).

This compound was once obtained when some hydroxyperezone, prepared in the usual way, was dissolved in xylene and set aside in a corked vessel for several months. It was, however, always found in moderate quantities when preparing perezinone,  $C_{15}H_{16}O_3$  (Mylius, *loc. cit.*, p. 944), and was isolated as follows. Concentrated sulphuric acid was poured on to hydroxyperezone, and the mixture warmed to  $60-70^\circ$  for five minutes, the liquor was cooled, and water cautiously added, keeping the temperature of the solution below  $45^\circ$ , until a slight, permanent cloud appeared. After some time a dark green substance crystallised out, and was recrystallised from alcohol with the addition of animal charcoal. A mixture of the above-mentioned substance, which does not melt at  $300^\circ$ , and another compound was obtained in this way, and the latter was separated by means of benzene, and crystallised from this solvent, with the addition of light petroleum, in clusters of orange needles, melting at  $166-167^\circ$  (corr.). On further dilution of the acid mother liquors, perezinone crystallised out, and after recrystallisation was obtained pure, melting at  $143-144^\circ$ . Compound,  $166-167^\circ$  (melt at  $100^\circ$ ):

0.1403 gave 0.3565  $CO_2$  and 0.0764  $H_2O$ .  $C = 69.2$ ;  $H = 6.0$ .

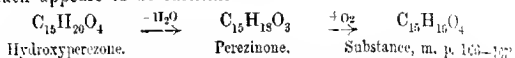
0.0980 .. 0.2428  $CO_2$  .. 0.0506  $H_2O$ .  $C = 69.0$ ;  $H = 5.9$ .

$C_{15}H_{16}O_4$  requires  $C = 69.2$ ;  $H = 6.1$  per cent.

It is readily soluble in most organic solvents and insoluble in water. It is instantly soluble in dilute sodium hydroxide or sodium carbonate, giving the same violet coloration as perezone (perezinone gives a yellow colour), and is reprecipitated unchanged by acids. An acetic acid solution is quickly rendered colourless by reducing with zinc dust, but is soon oxidised back by contact with the air. These two facts point to the compound being a hydroxyquinone

like perezone, and as Millon's reagent gives a deep red colour, only one phenolic hydroxyl group is present in the molecule. Ferric chloride gives a purple-brown colour to an acetone solution. It does not combine with aniline, a fact which indicates that all positions in the ring are already occupied.

Perezinone,  $C_{15}H_{15}O_3$ , which is formed by loss of water from hydroxyperezone,  $C_{15}H_{20}O_4$ , does not itself combine with aniline for the same reason, and it is probable that the compound in question is formed from perezinone by replacement of two hydrogen atoms of one of the side-chains by an atom of oxygen, since the ring system in each appears to be identical:



When this substance, melting at  $166-167^\circ$ , is boiled for half an hour with an alcoholic solution of aniline, it is entirely converted into the substance which does not melt below  $300^\circ$ , the second by-product in the preparation of hydroxyperezone. This interesting change has not, however, been investigated further.

*Substance which does not melt below  $300^\circ$ .*—This substance was first observed by Anschütz and Leather as an impurity in hydroxyperezone. It may be separated from crude hydroxyperezone by fractional crystallisation from alcohol, in which it is less soluble than the latter, and, as mentioned above, it is also obtained in the preparation of perezinone, and by the action of alcoholic aniline on the substance  $C_{15}H_{16}O_4$ , melting at  $166-167^\circ$ . It crystallises from alcohol in bronze-coloured needles, and gives on analysis figures which are not readily to be explained. It contains no nitrogen:

0.1036 gave 0.2612  $CO_2$  and 0.0510  $H_2O$ .  $C=68.76$ ;  $H=5.5$ .

0.1058 „ 0.2660  $CO_2$  „ 0.0516  $H_2O$ .  $C=68.6$ ;  $H=5.7$ .

It is readily soluble in dilute sodium hydroxide, giving a red solution, and also in sodium carbonate. No colour is given with ferric chloride. Zinc dust and acetic acid easily reduce it to a colourless solution, which, however, rapidly resumes its former red colour on keeping in the air, thus resembling perezone; like the latter it is also not reduced by sulphurous acid. The quinone structure is therefore probably present.

#### *Attempted Acetylation of Hydroxy- and Amino-perezone.*

Anschütz and Leather failed to obtain a crystalline acetyl derivative of hydroxyperezone, and the author has found that, although acetic anhydride appears to react with this substance, only a pale coloured glue could be obtained. This glue closely resembled that produced by the action of acetic anhydride on perezone, and the fact that both were without any characteristic

quinone colour makes it conceivable that a rearrangement of the atoms in the molecule of hydroxyperezone is brought about by this treatment just as occurred in the case of perezone itself. It was therefore much to be regretted that a crystalline compound could not be obtained in order to obtain further evidence on this point.

Aminoperezone with acetic anhydride also gave a similar clear gum, from which no crystalline product could be obtained. When boiled in alcoholic solution with zinc chloride, aminoperezone forms an additive product, which crystallises from alcohol as a blue powder, and contains chlorine. It appears to be the *zincichloride*:

0.1206 gave 0.0148 ZnO. Zn = 9.86.

$(C_{17}H_{21}O_3N)_2ZnCl_2$  requires Zn = 9.87 per cent.

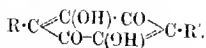
#### *Various Experiments with Perezone.*

Attempts were made to isolate the colourless reduction product through its acetyl compound by boiling perezone in acetic anhydride with zinc dust. In all cases, however, the whole of the acid was recovered unchanged, being oxidised back by the air. Many experiments were made with a view to obtaining some clue to the constitution of the side-chains by oxidising with potassium permanganate, potassium dichromate, etc., and by fusion with potassium hydroxide, but no crystalline compound could ever be isolated. A non-crystalline acid portion, which had a strong odour resembling that of butyric acid, and traces of a phenolic substance were the only indications obtained during these oxidations and fusion experiments; also a characteristic sweet odour was always noticed, which somewhat resembled that of amyl acetate.

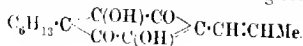
Attempts at benzoylating perezone by the normal Schotten-Baumann method were entirely without success, and this is not surprising, seeing that attempts at acetylation by boiling with acetic anhydride and fused sodium acetate or acetyl chloride under ordinary pressure were also unsuccessful.

#### *Addendum.*

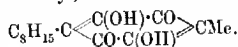
Fichter, Jetzer, and Leepin (*Annalen*, 1913, **395**, 15) have now shown that hydroxyperezone has the properties of a 3:6-dihydroxy-2:5-dialkyl-*p*-benzoquinone:



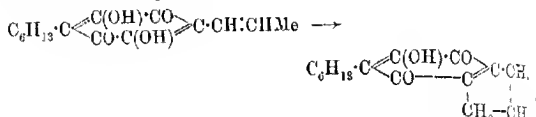
and that it yields  $\alpha\beta$ -diketobutyric acid on treatment with ozonised oxygen. The latter result is accounted for by the suggestion that  $R' = \text{propenyl}$ , and  $R$  must then be hexyl, since  $R + R' = C_6H_{17}$ . Hydroxyperezone would then have the following constitution:



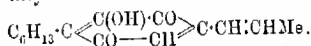
It should be pointed out, however, that the formation of  $\alpha\beta$ -diketobutyric acid can be explained at least equally well by the assumption that  $R^1$  = methyl, when  $R$  would be octenyl, as follows.



Fichter, Jetzer, and Leepin explain the formation of perezinone, which is obtained by the dehydration of hydroxyperezone with concentrated sulphuric acid by the assumption that the following condensation takes place:



Since perezone does not undergo a similar dehydration with sulphuric acid, they ascribe to it the formula:



The evidence for the nature of the side-chains is, however, inconclusive, and this constitutional formula can therefore only be accepted with reserve.

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### CXVII.—*The Absorption Spectra of Various Derivatives of Benzene.*

By JOHN EDWARD PURVIS and NIAL PATRICK McCLELAND.

THE aim of this communication is to describe a series of observations of the absorption spectra in the ultra-violet regions of various derivatives of benzene in various physical conditions, and particularly the vapours of these substances, and to see how far the absorption is modified when different side chains are introduced, and especially the nitro-group.

The substances examined were the following: phenol, catechol, guaiacol, *o*-, *m*-, and *p*-cresols, *o*-, *m*-, and *p*-chlorophenols, *o*-, *m*-, and *p*-chloroanilines, benzaldehyde, acetophenone, benzophenone, nitrobenzene, *o*-, *m*-, and *p*-dinitrobenzenes, *o*-, *m*-, and *p*-nitro toluenes, *o*-nitrophenol, *o*- and *p*-nitroanisoles, *o*-nitroaniline, *o*-, *m*- and *p*-nitrobenzaldehydes, and nitromethane. In some cases it was impossible to examine the vapours of the isomerides because of their comparatively high melting points.

The experimental methods have been described before. The cadmium spark and the acetylene lamp were used as sources of the radiant energy.

*Phenol*.—Hartley, Dobbie, and Lauder (T., 1902, **81**, 929) showed that solutions of the substances had one strong band, the head of which is at about  $1/\lambda$  3670 ( $\lambda$  2720). This was confirmed later by Baly and Ewbank (T., 1905, **87**, 1347).

The vapour of this substance has been studied by the authors, and the following phenomena were observed at the temperatures of  $45^\circ$  and  $60^\circ$  in a 200 mm. tube.

*Abbreviations*: v.w. = very weak; w. = weak; f.str. = fairly strong; str. = strong; diff. = diffuse.

	45° 70 mm.	45° 70 mm.	60° 100 mm.	60° 100 mm.
	$\lambda$	$\lambda$	$\lambda$	$\lambda$
A	2812 v.w.	2841 v.w.	2812 v.w.	2555 str.
	2794 "	2638 "	2801 "	2560 w.
	2790 w.	*2631 f.str.	2794 "	2558 w.
	2784 v.w.	2631 v.w.	2788 w., wide	2552 w.
	2777 "	2630 "	2784 "	2549 w.
	2770 "	2628 "	2780 v.w.	2540 w.
	2771 "	*2625 str.	2777 "	2530 v.w.
	2766 w.	2623 v.w.	2775 ", wide	2529 "
	2761 w.	2618 w.	2769 w.	2521 "
	2757 v.w.	*2613 str.	2766 f. str.	2520 "
B	2745 w.	2611 w.	2761 "	2518 "
	2741 f.str.	2607 w.	(2760)	2516 "
	2740 v.w.	*2604 f. str.	to str.	2514 "
	2744 "	2603 w.	(2748)	2510 "
	2738 "	2597 "	2744 v.w.	2509 "
	2735 "	*2593 f.str.	2738 "	2504 "
	2732 "	*2580 str.	2735 "	2500 "
	2729 w.	2578 v.w.	2732 "	
	2725 w.	2575 "	2729 w.	General absorption began at $\lambda$ 2220
	2722 w.	*2572 f. str.	2725 w.	
C	2719 w.	2565 v.w.	2722 w.	53 bands.
	2716 w.	*2560 w.	2719 w.	
	2710 f.str.	2558 v.w.	2716 w.	General absorption began at $\lambda$ 2180.
	2708 w.	*2552 f. str.	2710 str., wide	
	2704 w.	2549 v.w.	(2704)	to very diff.
	2700 w.	*2540 "	(2670)	
	2695 w.	*2530 w.	(2670)	to very diff.
	2691 w.	2529 v.w.	2663	
	2688 str., wide	2521 "	2651	to very diff.
	2687 "	*2520 w.	2644	
D	2681 w.	2518 "	2641	to very diff.
	2677 w.	2516 "	2638	
	2672 str.	2514 "	2635	to very diff.
	2669 w.	2510 "	2625	
	2663 v.w.	2509 "	(2623)	to very diff.
	2659 "	2504 "	(2600)	
	2651 diff.	2500 "	2593	to very diff.
	2650 v.w.		2580	
	*2644 str.		2578	to very diff.
			2575	
			2572	to very diff.
			2569	
			2560	to very diff.
			2555	
			2552	to very diff.
			2549	
			2540	to very diff.
			2530	
			2529	to very diff.
			2521	
			2520	to very diff.
			2518	
			2516	to very diff.
			2514	
			2510	to very diff.
			2509	
			2504	to very diff.
			2500	
			2495	to very diff.
			2491	
			2488	to very diff.
			2487	
			2481	to very diff.
			2477	
			2472	to very diff.
			2469	
			2463	to very diff.
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			2451	to very diff.
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			2441	to very diff.
			2438	
			2435	to very diff.
			2425	
			2423	to very diff.
			2420	
			2400	to very diff.
			2393	
			2380	to very diff.
			2378	
			2375	to very diff.
			2372	
			2369	to very diff.
			2360	
			2355	to very diff.
			2352	
			2349	to very diff.
			2340	
			2330	to very diff.
			2329	
			2321	to very diff.
			2320	
			2318	to very diff.
			2316	
			2314	to very diff.
			2310	
			2309	to very diff.
			2304	
			2300	to very diff.
			2295	
			2291	to very diff.
			2288	
			2287	to very diff.
			2281	
			2277	to very diff.
			2272	
			2269	to very diff.
			2263	
			2259	to very diff.
			2251	
			2250	to very diff.
			2244	
			2241	to very diff.
			2238	
			2235	to very diff.
			2225	
			2223	to very diff.
			2220	
			2200	to very diff.
			2193	
			2180	to very diff.
			2178	
			2175	to very diff.
			2172	
			2169	to very diff.
			2160	
			2155	to very diff.
			2152	
			2149	to very diff.
			2140	
			2130	to very diff.
			2129	
			2121	to very diff.
			2120	
			2118	to very diff.
			2116	
			2114	to very diff.
			2110	
			2109	to very diff.
			2104	
			2100	to very diff.
			2095	
			2091	to very diff.
			2088	
			2087	to very diff.
			2081	
			2077	to very diff.
			2072	
			2069	to very diff.
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			2059	to very diff.
			2051	
			2044	to very diff.
			2041	
			2038	to very diff.
			2035	
			2025	to very diff.
			2023	
			2020	to very diff.
			2000	
			1993	to very diff.
			1980	
			1978	to very diff.
			1975	
			1972	to very diff.
			1969	
			1960	to very diff.
			1955	
			1952	to very diff.
			1949	
			1940	to very diff.
			1930	
			1929	to very diff.
			1921	
			1920	to very diff.
			1918	
			1916	to very diff.
			1914	
			1910	to very diff.
			1909	
			1904	to very diff.
			1900	
			1895	to very diff.
			1891	
			1888	to very diff.
			1887	
			1881	to very diff.
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			1851	to very diff.
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			1841	to very diff.
			1838	
			1835	to very diff.
			1825	
			1823	to very diff.
			1820	
			1800	to very diff.
			1793	
			1780	to very diff.
			1778	
			1775	to very diff.
			1772	
			1769	to very diff.
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			1755	to very diff.
			1752	
			1749	to very diff.
			1740	
			1730	to very diff.
			1729	
			1721	to very diff.
			1720	
			1718	to very diff.
			1716	
			1714	to very diff.
			1710	
			1709	to very diff.
			1704	
			1700	to very diff.
			1695	
			1691	to very diff.
			1688	
			1687	to very diff.
			1681	
			1677	to very diff.
			1672	
			1669	to very diff.
			1663	
			1659	to very diff.
			1651	
			1644	to very diff.
			1641	
			1638	to very diff.
			1635	
			1625	to very diff.
			1623	
			1620	to very diff.
			1600	
			1593	to very diff.
			1580	
			1578	to very diff.
			1575	
			1572	to very diff.
			1569	
			1560	to very diff.
			1555	
			1552	to very diff.
			1549	
			1540	to very diff.
			1530	
			1529	to very diff.
			1521	
			1520	to very diff.
			1518	
			1516	to very diff.
			1514	
			1510	to very diff.
			1509	
			1504	to very diff.
			1500	
			1495	to very diff.
			1491	
			1488	to very diff.
			1487	
			1481	to very diff.
			1477	
			1472	to very diff.
			1469	
			1463	to very diff.
			1459	
			1451	to very diff.
			1444	
			1441	to very diff.
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			1435	to very diff.
			1425	
			1423	to very diff.
			1420	
			1400	to very diff.
			1393	
			1380	to very diff.
			1378	
			1375	to very diff.
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			1321	to very diff.
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			1318	to very diff.
			1316	
			1314	to very diff.
			1310	
			1309	to very diff.
			1304	
			1300	to very diff.
			1295	
			1291	to very diff.
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			1287	to very diff.
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			1241	to very diff.
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			1235	to very diff.
			1225	
			1223	to very diff.
			1220	
			1200	to very diff.
			1193	
			1180	to very diff.
			1178	
			1175	to very diff.
			1172	
			1169	to very diff.
			1160	
			1155	to very diff.
			1152	
			1149	to very diff.
			1140	
			1130	to very diff.
			1129	
			1121	to very diff.
			1120	
			1118	to very diff.
			1116	
			1114	to very diff.
			1110	
			1109	to very diff.
			1104	
			1100	to very diff.
			1095	
			1091	to very diff.
			1088	
			1087	to very diff.
			1081	
			1077	to very diff.
			1072	
			1069	to very diff.
			1063	
			1059	to very diff.
			1051	
			1044	to very diff.
			1041	
			1038	to very diff.
			1035	
			1025	to very diff.
			1023	
			1020	to very diff.
			1000	
			993	to very diff.
			980	
			978	to very diff.
			975	
			972	to very diff.
			969	
			960	to very diff.
			955	
			952	to very diff.
			949	
			940	to very diff.
			930	
			929	to very diff.
			921	
			920	to very diff.
			918	
			916	to very diff.
			914	
			910	to very diff.
			909	
			904	to very diff.
			900	



It is seen that the absorption spectrum of the vapour of phenol consists of a maximum number of 76 bands, which, with increasing temperature, coalesce into a single band resembling that observed in the solution. The spectrum does not show any resemblance to that of benzene, as described and measured by Hartley (*Phil. Trans.*, 1907, **A**, 208, 475). The hydroxyl group has entirely changed the type of vibration of the system, as does the amino-group in aniline (Purvis, T., 1910, **97**, 1546).

The most marked feature of the spectrum is the long series of equidistant bands marked \* in the table. These bands are very similar in appearance (save that the more refrangible ones are weaker), and are situated about 10 units apart. If the spectra of phenol and of anisole (Purvis and McClelland, T., 1912, **101**, 1514) be compared it will be found that these bands, with only two exceptions, appear in the two spectra. The anisole bands are, however, slightly wider than those in phenol. The two spectra show very close resemblance in most respects, and, with the dispersion used, it does not appear that there is any appreciable shift.

It should be added that the spectrum of anisole (Baly and Ewbank, *loc. cit.*), in solution, is described as having two bands, whereas that of phenol has only one.

*Catechol*.—Hartley has shown (T., 1888, **53**, 651) that solutions of the substance have one large strong band, the head of which is about at  $1/\lambda 3660$  ( $\lambda 2730$ ).

The substance was placed in a 100 mm. tube, which was exhausted, so that the inside pressure was about 12 mm. It was then examined at various temperatures, and the following phenomena were observed:

90°.	100°.
$\lambda$	
2806 w.	As described at 90°, but the bands were stronger.
2804 v.	
2797 w.	
2794 w.	General absorption began at $\lambda 2250$ .
2789 } w. diff.	6 bands.
to	
2784 }	
2736 }	
General absorption began at $\lambda 2240$ .	
6 bands.	

*Gumacul*.—Baly and Ewbank (*loc. cit.*) showed that the solution of the substance has one band, the head of which is at about  $1/\lambda 3610$  ( $\lambda 2770$ ).

As the melting point of the substance is considerably lower than that of catechol, its vapour was much more easily examined. The

substance was placed in a 200 mm. tube, and examined at various temperatures and pressures. The following phenomena were observed:

P.	60°.	75°.	90°.
823 mm.	863 mm.	893 mm.	923 mm.
The rays were weak	$\lambda$	2841 v.w., diff.	Rays were absorbed between $\lambda$ 2880 and $\lambda$ 2495
at $\lambda$ 2797	2833 v.w., diff.	2840	
and $\lambda$ 2786	2822 " "	to } strong band.	
$\lambda$	2816	2578	
2754 v.w.	to } str., diff.	General absorption began at $\lambda$ 2280.	General absorption began at $\lambda$ 2400.
2725 v.w., diff.	2783		
2700 w.			
2685 f.str., matr.	The rays were then weakly absorbed, but the following bands showed through:	1 weak band and 1 very strong band.	1 strong band.
2673 w. matr.			
General absorption, began at $\lambda$ 2450			
6 bands.	2754 w.		
	2744		
	to } v. diff.		
	2697		
	General absorption began at $\gamma$ 2240.		
	4 bands and 1 stronger band.		

There are therefore a series of fine bands in the vapour of the substance, which, at the higher temperatures and pressures, coalesce upon a single large band comparable with the solution band. The total number of bands is much less than was found in the vapour of phenol.

*Quinol.*—Hartley and Leonard (T., 1909, 95, 34) describe a narrow band at  $\lambda$  2538, and broad bands between  $\lambda$  2396 to 2332 and  $\lambda$  3080 to 2575 in the vapour spectrum of this substance.

*o*-, *m*-, and *p*-*Cresols*.—The absorption spectra of solutions of each of these substances have been shown by Hartley (T., 1888, 53, 641) to exhibit one large band, the head of which is at about  $\lambda$  3650 ( $\lambda$  2740).

*o*-*Cresol*.—The absorption spectra of the vapour of the substance in a 200 mm. tube and at various temperatures and pressures showed the following phenomena:

45°.	60°.
829 mm.	859 mm.
$\lambda$	$\lambda$
2825 w.	2845 w.
The rays were weak between 2775 and 2757.	2781
	to } f. str.
	2751
	2743 str.
	2732
2695 v.w.	to }
2686 f.str.	2580
2673	
General absorption began at $\lambda$ 2190.	General absorption began at $\lambda$ 2225.
5 bands	3 weaker bands and 1 large band.

*m-Cresol*.—The absorption spectra of the vapour of the substance in a 200 mm. tube and at various temperatures and pressures showed the following phenomena:

45°.	60°.
835 mm.	865 mm.
$\lambda$	$\lambda$
2778 f. str.	2820 } str.
2771 ..	to }
2766 ..	2760 } str.
2754 v.w.	2754 v.w., diff.
2732 }	2745 }
to } v.w., diff.	to } v. str.
2691 }	2568 }
2684 v.w., wide	
2641 v.w.	General absorption
2638 ..	began at $\lambda$ 2250.
2633 ..	
2630 ..	2 weaker bands and
2623 ..	large strong band.
2618 ..	

General absorption  
began at  $\lambda$  2190.

12 bands.

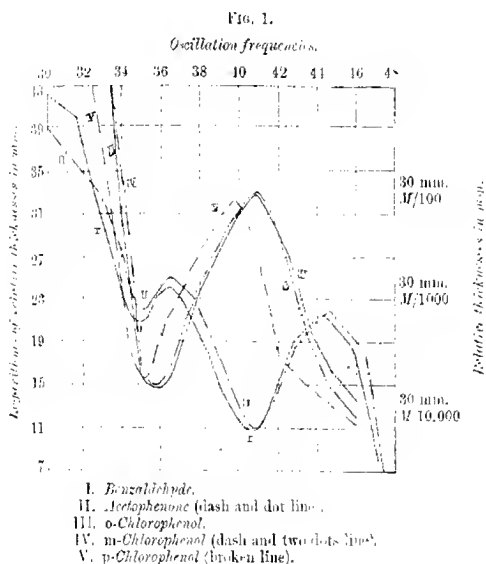
*p-Cresol*.—The absorption spectra of the vapour of the substance in a 200 mm. tube, and at various temperatures and pressures, showed the following phenomena:

45°.	45°.	60°.	60°.
296 mm.	296 mm.	326 mm.	326 mm.
$\lambda$	$\lambda$	$\lambda$	
2850 v.w.	2699 v.w.	2869 v.w.	The rest of the bands were a- described at 45° but at 60° they appeared stronger.
2841 v.w., narr.	2680 }	2850 f. str.	
2840 ..	* to } w., wide	2841 w.	
2828 str. diff. on	2664 }	2840 w.	
less re-	2647 }	*2837 }	
frangible	* to } w., wide	to } str.	
side	2630 }	2820 }	
2823 w.	2626 v.w., narr.	2823 w.	General absorption $\lambda$ 2260.
*2807 } str. diff. on	2623 ..	2812 v.w.	
to } less re-	2620 ..	2808 ..	
2794 } frangible	2618 }	*2807 }	23 bands.
side.	* to } v.w., diff.	to } f. str.	
*2775 } str. diff. on	2603 }	2794 }	
to } less re-	2590 }	2782 v.w., diff.	
2760 } frangible	* to } v.w., diff.	2778 ..	
side.	2577 }	*2775 }	
2733 w.		to } str.	
2728 v.w.	General absorption	2759 }	
2709 }	$\lambda$ 2200.	2741 }	
* to } w., wide		to } f. str.	
2702 }	18 bands.	2732 }	

The bands marked \* are wide and sharp on the more refrangible side. They appear to correspond with the bands marked similarly in phenol, but are much wider.

The vapour bands are wholly unlike the single solution band of each of these substances, although at the higher temperatures and pressures there is a tendency for these bands to coalesce into one large band not unlike the solution band. Also, it should be noticed that the vapour bands in each of the substances are much fewer in number than in phenol vapour; the spectrum of the para-derivative alone shows a marked resemblance to that of the parent substance; and that of the meta-derivative, and, still more, that of the ortho-compound, appear to be quite unlike it.

*o*-, *m*-, and *p*-Chlorophenols.—Alcoholic solutions of various



strengths were examined, and a large band was found in solutions of each of the substances. The absorption curve (Fig. 1, III, IV, and V) show that the head of the curve of the ortho-compound is at  $1/\lambda$  3580 ( $\lambda$  2790); that of the meta-compound is at  $1/\lambda$  3590 ( $\lambda$  2784); and that of the para-compound at  $1/\lambda$  3500 ( $\lambda$  2856). The band of the *p*-compound is therefore shifted a little more towards the red end of the spectrum than the bands of the other isomerides. The general form of the bands is very similar to the large band of phenol.

*o*-Chlorophenol.—The absorption spectra of the substance in a 200 mm. tube at various temperatures and pressures showed the following phenomena:

30°.	30°.	45°.
813 mm.	813 mm.	839 mm.
$\lambda$	$\lambda$	$\lambda$
2809 f. str.	2653 w., diff.	2870 v.w., diff.
2807 v.w.	2643 "	2853 w.
2804	2630 "	2840 w.
to	2623 "	2830
2775 } str.	2616 "	to
2787 v.w.	2612 "	2584 } v. str.
2763 "	2608 "	
2760 "	2604 "	General absorption
2755 "	2601 "	began at $\lambda$ 2270.
2752 "	2593 "	
2735 w.	2581 "	3 narrow bands and
2734 } w. diff.	2578 "	1 strong band.
to	2571 "	
2677		
2671 "	General absorption	
	began at $\lambda$ 2240.	

21 bands.

*m*-Chlorophenol.—The absorption spectra of *m*-chlorophenol in a 200 mm. tube at various temperatures and pressures:

45°.	60°.	60°.
839 mm.	869 mm.	869 mm.
$\lambda$	$\lambda$	$\lambda$
2809 v.w.	2815 v.w.	2725 w.
2805 v.w., nar.	2809 w.	2722 w.
2802 w., wide	2805 w.	2717 w.
2798 w.	2802 f. str.	2713 v.w., diff.
2795 f. str.	2798 "	2707 v.w.
2789 v.w.	2795 str.	2704 "
2784 f. str.	2792 w.	2692 "
2781 v.w.	2789 w.	2685 "
2756 "	2784 str.	2678 "
2733 "	2781 w.	2674 "
2725 "	2777 v.w.	2664 "
2717 "	2756 f. str.	2657 "
2653 "	2743 w.	
General absorption	2738 v.w.	General absorption
began at $\lambda$ 2130.	2733 f. str.	began at $\lambda$ 2235.
	2728 v.w.	

13 bands.

28 bands.

*p*-Chlorophenol.—The absorption spectra of *p*-chlorophenol in a 200 mm. tube at various temperatures and pressures:

45°.	45°.
839 mm.	839 mm.
$\lambda$	$\lambda$
2875 v.w.	2785 v.w.
2873 w.	2781 "
2844 v.w.	General absorption
2841 "	began at $\lambda$ 2150.

6 bands.

60°. 569 mm.	60°. 869 mm.	60°. 869 mm.
$\lambda$	$\lambda$	$\lambda$
2816 w.	2813 w.	2753 v.w.
2865 v.w.	2809 w.	2722 "
2897 "	2807 w.	2707 v.w., wide
2894 "	2803 w.	2704 " "
2882 "	2794 v.w.	2698 " "
2875 f. str.	2789 v.w.	2686 " "
2873 "	2785 f.str.	
2870 f.str.	2781 v.w.	General absorption began at $\lambda$ 2260.
2865 w.	2779 "	
2866 v.w.	2770 "	
2860 "	2756 w.	
2849 w.		39 bands.
2844 w.		
2841 w.		

Therefore the absorption spectra of the vapours of *o*-, *m*-, and *p*-chlorophenols are again wholly different from those of the one band of each of the solutions; but, at the higher temperatures and pressures, there is a tendency for the vapour bands to coalesce into one large band which is similar to the solution band. The total number of bands is considerably reduced as compared with those of phenol, as a consequence of the introduction of the chlorine atom. Of the three isomerides, the spectrum of the *para*-, and still more of the *meta*-compound, appears to resemble that of the parent substance; but there is a shift of about 50 units towards the less refrangible part of the spectrum.

*o*-, *m*-, and *p*-Chloroanilines.—Baly and Ewbank (T., 1905, 87, 1355) showed that in acid solutions of *o*-chloroaniline there was a rapid extension of the rays between about  $1/\lambda$  3700 to  $1/\lambda$  4300 ( $\lambda$  2700 to  $\lambda$  2320); in *m*-chloroaniline there was a band the head of which was at  $1/\lambda$  3700 ( $\lambda$  2700); and in *p*-chloroaniline there were two bands at  $1/\lambda$  3650 ( $\lambda$  2740), and at  $1/\lambda$  3750 ( $\lambda$  2660); whereas in neutral solutions of each of these substances the *ortho*-compound showed a band at  $1/\lambda$  3450 ( $\lambda$  2900), the *meta*-compound one at  $1/\lambda$  3410 ( $\lambda$  2930), and the *para*-compound at  $1/\lambda$  3360 ( $\lambda$  2980).

*o*-Chloroaniline.—The absorption spectrum of the vapour of *o*-chloroaniline in a 200 mm. tube at various temperatures and pressures:

30°. 801 mm.	30°. 801 mm.
$\lambda$	$\lambda$
2880 w.	2817 v.w., diff.
2970 v.w., narr.	2809 " "
2956 v.w.	
2954 "	The rays were then trans- mitted to $\lambda$ 2370, beyond which only the strong C l. lines were visible.
2946 "	
2938 "	
2905 w., wide	
2880 "	12 bands.
2869 v.w.	
2825 v.w., diff.	

## 1096 PURVIS AND McCLELAND: THE ABSORPTION SPECTRA

45°.	45°.
827 mm.	827 mm.
$\lambda$	$\lambda$
2895 w., narr.	2948 } f.str.
2878 f.str., wide	to
2870 v.w., narr.	2945 }
2866 }	
to diffuse	
2860 }	
2858 }	
to f.str.	
2850 }	

Rays were then absorbed to  $\lambda$  2775. They were then transmitted to  $\lambda$  2450, where general absorption began.

7 weaker bands and 1 large band.

*m*-Chloroaniline.—The absorption spectrum of the vapour of *m*-chloroaniline in a 200 mm. tube at various temperatures and pressures:

45°.	45°.	60°.	60°.
829 mm.	829 mm.	859 mm.	859 mm.
$\lambda$	$\lambda$	$\lambda$	$\lambda$
2895 v.w., narr.	2898 v.w.	3002 v.w.	2920 w.
2881 w., narr.	2893 "	3000 w., narr.	2914 w.
2878 f.str.	2890 w.	2995 "	2910 f.str., wide
2861 w.	2875 v.w.	2986 "	2906 "
2856 w.	2870 "	2981 f.str.	2898 w.
2852 w.	2857 v.w., diff.	2978 str.	2893 w.
2846 w.	2849 "	2963 v.w.	2890 str.
2841 w.	2846 "	2961 f.str.	
2838 v.w.		2956 "	Then faint absorption to $\lambda$ 2750.
2832 f.str.	General absorption began at $\lambda$ 2260.	2952 str., wide	
2827 v.w.		2946 w.	
2824 "		2941 mod. w.	General absorption began at $\lambda$ 2490.
2820 "	24 bands.	2938 "	
2814 "		2932 str.	
2810 w.		2927 w.	28 bands and 1
2806 w.		2924 w.	strong band.

*p*-Chloroaniline.—The absorption spectra of the vapour of *p*-chloroaniline in a 200 mm. tube at various temperatures and pressures:

60°.	75°.
857 mm.	887 mm.
$\lambda$	$\lambda$
3174 w.	3174 w.
3147 f.str., diff.	3155 }
3144 w., narr.	to str., wide.
2969 f.str.	3010 }
	3035 w., diff.
General absorption began at $\lambda$ 2500.	3062 to 2860 a broad diffuse band, the less refrangible edge of which is apparently broken up into smaller bands, but the nature of the cadmium spark in this region makes accurate measurement impossible.
4 bands.	

4 weaker bands and 1 large band.

The vapour of each of these substances hence shows a series of free bands completely different from their solution; but the number of vapour bands in each substance is less than in the vapour of aniline. The striking shift of the vapour bands of these aniline compounds towards the red end, as compared with other benzene derivatives, is comparable with that noticed in the vapour of aniline itself (Purvis, *loc. cit.*), and this appears to be a clear indication that the amino-group is a powerful oscillation centre.

As in the phenols, the meta-derivative spectroscopically resembles the parent substance more than do the other isomerides, whilst the ortho- is quite distinct. The shift due to the chlorine atom in the meta-chloroaniline is about 37 units, and when this allowance is made it is found that a large number of the principal bands in the spectrum correspond with similar bands in aniline. Further, the bands of *m*-chloroaniline are much sharper than those of the other isomerides.

*Benzaldehyde*.—Baly and Collie (T., 1905, 87, 1332) found a band at  $1/\lambda$  3500 ( $\lambda$  2850) in *M*/1000-alcoholic solutions. We have repeated these experiments and also investigated the absorption of *M*/10,000-solutions, and find that besides the less refrangible band noticed by Baly and Collie in *M*/1000-solutions, there is a large band the head of which is at  $1/\lambda$  4070 ( $\lambda$  2456) in *M*/10,000-solutions. The absorption curve has been drawn (Fig. 1, I). The benzaldehyde was redistilled under diminished pressure and dissolved in alcohol which had been previously boiled in order to hinder the oxidation to benzoic acid. The absorption spectra of the vapour of benzaldehyde at various temperatures and pressures in a 200 mm. tube showed the following phenomena. The vapour of this substance was examined both with the acetylene light and also with the cadmium spark. Owing to the ease with which it oxidises, the vapour was examined in an atmosphere of nitrogen. Further, the vapour of carefully purified benzoic acid was found to show none of the bands given below:

30°. 799 mm.	30°. 799 mm.	30°. 799 mm.	30°. 799 mm.
$\lambda$	$\lambda$	$\lambda$	$\lambda$
2560 w.	2784 w.	2711 v. w., diff.	2620 v. w.
2579 f. str.	2776 f. str.	2707 " "	2615 "
2590 "	2771 w.	2701 v. w.	
2591 "	2762 f. str.	2688 "	The rays were also absorbed between $\lambda$ 2455 and $\lambda$ 2160.
2592 "	2757 w.	2680 "	
2595 "	2752 v. w.	2667 "	
2596 "	2743 "	2653 "	
2591 w.	2729 v. w., diff.	2633 "	General absorption began at $\lambda$ 2150.
2590 f. str.	2720 " "	2622 "	
2595 w.			

31 bands.



## 1098 PURVIS AND McCLELAND: THE ABSORPTION SPECTRA

45°. 825 mm.	45°. 825 mm.	45°. 825 mm.	45°. 825 mm.
$\lambda$	$\lambda$	$\lambda$	$\lambda$
3700 v.w.	*2822 str., wide	2752 w.	2633 v.w.
3587 "	*2815 "	2743 w.	2633 "
—	*2807 "	2729 v.w., diff.	2622 "
2894 v.w.	2801 w.	2720 " "	2620 "
2886 "	*2796 f.str.	2711 " "	2615 "
2877 "	2790 w.	2707 "	
2870 "	2784 w.	2701 w.	General absorption began at $\lambda$ 2580.
2860 f. str.	*2776 str.	2688 w.	
*2850 v. str.	2771 w.	2680 v.w.	
*2840 "	*2762 str.	2667 w.	35 bands.
*2831 str.	2757 w.		

75°. 885 mm.	75°. 885 mm.
$\lambda$	$\lambda$
3700 v.w.	*2894 f.str.
3695 f.str.	*2886 "
3650 v.w.	2885 w.
3608 "	
3550 "	General absorption began at $\lambda$ 2880.
3515 f.str.	
2949 v.w.	
2941 "	12 bands.
2929 w.	

The bands marked \* are very similar in appearance; they are diffuse on the less refrangible side, and are not unlike the similar series of bands in phenol. The vapour of the substance, therefore, showed two series of fine bands which are quite different from the less refrangible solution band. On the other hand, the more refrangible vapour band between  $\lambda$  2430 and  $\lambda$  2220 is comparable with the large solution band at  $1/\lambda$  4070 ( $\lambda$  2456) in that it does not break up into a series of finer bands; and differs from it mainly in position. However, the series of fine bands on the border of the visible region does not appear to be strong enough to appear in the solution spectrum.

*Acetophenone.*—Baly and Collie (*loc. cit.*) noticed a rapid extension of the rays between  $1/\lambda$  3500 ( $\lambda$  2856) and  $1/\lambda$  3800 ( $\lambda$  2630) in  $M/1000$ -alcoholic solutions. The authors have repeated these experiments and also investigated the absorption of  $M/10,000$ -solutions, and find that, besides the much less refrangible band in  $M/1000$ -solutions noticed by Baly and Collie, there is a large band at  $1/\lambda$  4080 ( $\lambda$  2450) in  $M/10,000$ -solutions. The absorption curve has been drawn (Fig. 1, II).

The absorption spectra of the vapour of acetophenone at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

30°.	60°.
501 mm.	857 mm.
$\lambda$	$\lambda$
The rays were absorbed	2833
between $\lambda$ 2420 and	to
$\lambda$ 2200, and then weakly	2816 } diff.
transmitted to $\lambda$ 2150,	2763
where general absorption	to
began.	2709 } diff.

General absorption began at  $\lambda$  2460.

The vapour of acetophenone thus consists of two principal bands, the less refrangible of which breaks up into two smaller bands. The vapour was also examined for bands in the neighbourhood of the visible part of the spectrum, but no absorption was detected. It is seen that the number of bands found in the vapour of benzaldehyde has been considerably decreased.

*Benzophenone*.—The authors (T., 1912, 101, 1514) found two solution bands at  $1/\lambda$  2960 ( $\lambda$  3360) and  $1/\lambda$  3980 ( $\lambda$  2510) respectively. The latter was visible in  $M/10,000$ -alcoholic solutions, and the former in  $M/100$ -solutions.

The absorption spectra of the vapour at various temperatures and pressures showed the following phenomena:

	Pressure	
	in mm.	
60	227	The rays were absorbed between $\lambda$ 2530— $\lambda$ 2320, and then weakly transmitted to about $\lambda$ 2150.
100	948	The rays were transmitted to $\lambda$ 2350.

The authors were not successful in obtaining sufficient vapour in the tube to show a vapour band corresponding with the very weak solution band at  $\lambda$  3360. The more refrangible band showed no signs of breaking up into a series of finer bands, and it corresponds with the solution band  $\lambda$  2510. It should also be noticed that all the fine bands found in the vapour of benzaldehyde have completely disappeared.

*Nitrobenzene*.—Paner (*Ann. Phys. Chem.*, 1897, [iii], 61, 375) found no bands in alcoholic solutions of this substance. Baly and Collie (T., 1905, 87, 1344) found a weak band as indicated by a rapid extension of the transmitted rays between  $1/\lambda$  3700 and  $1/\lambda$  4200 ( $\lambda$  2702— $\lambda$  2380) in  $M/1000$ -alcoholic solutions. The authors have repeated the experiments, and the absorption curve of this very weak band has been drawn (Fig. 2, I) in order to compare it with the dinitrobenzenes.

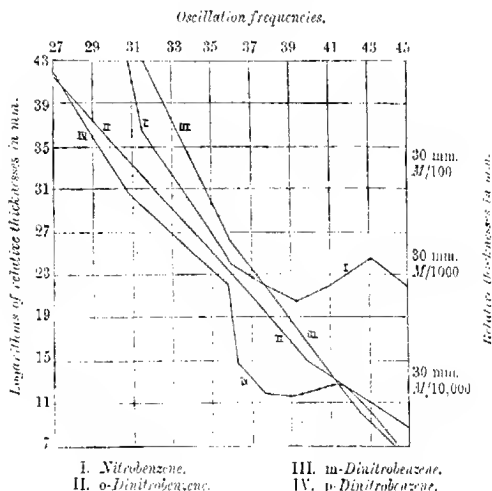
The absorption spectrum of the vapour of nitrobenzene at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure		
P, in mm.		
30	797	The rays were absorbed between about $\lambda$ 2500— $\lambda$ 2340 and then transmitted to about $\lambda$ 2150. The series of Cd lines $\lambda$ 2329— $\lambda$ 2144 were fairly well marked.
75	883	The rays were transmitted to about $\lambda$ 2900.

The vapour therefore showed a weak band comparable with the weak solution band. All the series of fine bands in benzene vapour described and measured by Hartley (*loc. cit.*) have completely disappeared.

*o*-, *m*-, and *p*-Dinitrobenzenes.—Alcoholic solutions of each of these substances were examined, and their absorption curves drawn.

FIG. 2.



It will be noticed (Fig. 2, II, III, and IV) that *o*- and *m*-dinitrobenzenes show no bands, whereas *p*-dinitrobenzene shows a very faint band the head of which is at about  $1/\lambda$  3900 ( $\lambda$  2563). The vapours of the dinitrobenzenes were not investigated.

It is interesting to note that Hantzsch and Picton (*Ner.*, 1909, 42, 2119) found no bands in solutions of trinitrobenzene.

*o*-Nitrotoluene.—Baly, Tuck, and Marsden (*T.*, 1910, 97, 571) state that solutions of the substance exhibit a band the head of which is at about  $1/\lambda$  4000 ( $\lambda$  2450).

The absorption spectrum of *o*-nitrotoluene vapour at various

temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure		
t.	in mm.	
39	810	The rays were transmitted to $\lambda$ 2150; but they were weak between about $\lambda$ 2500— $\lambda$ 2370.
45	840	The rays were transmitted to $\lambda$ 2590 and then absorbed to about $\lambda$ 2350; the series of Cd lines $\lambda$ 2320— $\lambda$ 2191 were well marked, as well as Cd 2573.
69	870	The rays were transmitted to $\lambda$ 2900, but the Cd lines $\lambda$ 2880 and $\lambda$ 2748 were just visible.

There was therefore one weak vapour band comparable with the solution band; but there was no resolution of the band into a series of fine bands. The less refrangible regions to about  $\lambda$  3200 were also examined by using the continuous spectrum of an acetylene lamp, but no bands were observed.

*m-Nitrotoluene*.—Baly, Tuck and Marsden (*loc. cit.*) state that solutions of the substance exhibit a band the head of which is at about  $1/\lambda$  3800 ( $\lambda$  2630). The absorption spectrum of *m*-nitrotoluene vapour at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure		
t.	in mm.	
45	830	The rays were absorbed between $\lambda$ 2560— $\lambda$ 2300 and then transmitted to about $\lambda$ 2140.
90	920	The rays were transmitted to $\lambda$ 3900.

There was therefore a single vapour band comparable with the solution band.

*p-Nitrotoluene*.—Baly, Tuck and Marsden (*loc. cit.*) found a band in solutions of the substance the head of which was at  $1/\lambda$  3600 ( $\lambda$  2780). The absorption spectrum of the vapour of *p*-nitrotoluene at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure		
t.	in mm.	
60	870	The rays were absorbed between $\lambda$ 2650— $\lambda$ 2360, and then transmitted to $\lambda$ 2144. The Cd line 2573 was visible.
90	930	The rays were transmitted to $\lambda$ 2900.

There was therefore a single vapour band comparable with the solution band. All the finer vapour bands of toluene described and measured by Hartley (*loc. cit.*) have completely disappeared in the vapours of *o*-, *m*-, and *p*-nitrotoluenes.

*o-Nitrophenol*. Baly, Tuck, and Marsden (*loc. cit.*) found two bands in solutions of the substance the heads of which were  $1/\lambda$  2900 ( $\lambda$  3440) and  $1/\lambda$  3600 ( $\lambda$  2770) respectively.

The absorption spectrum of the vapour of the substance at various

temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure °C. in mm.		
45	810	The rays were weakly absorbed between about $\lambda$ 3456— $\lambda$ 3100 and again between about $\lambda$ 2730— $\lambda$ 2590; and then transmitted to about $\lambda$ 2190.
60	870	The rays were absorbed between about $\lambda$ 3800— $\lambda$ 3020 and then transmitted to about $\lambda$ 2800. The Cd line 2748 was just visible.
75	900	The rays were absorbed between $\lambda$ 3750— $\lambda$ 2990 and then weakly transmitted to $\lambda$ 2900.
90	930	The rays were transmitted to $\lambda$ 2850; beyond which there was complete absorption.

The less refrangible band was also examined at the above temperatures and pressures by means of the continuous spectrum of an acetylene lamp; but there was no resolution of the band into a series of finer bands.

The two vapour bands are, therefore, comparable with the two solution bands, except in position. All the finer bands found in the vapour of phenol have completely disappeared.

*o*-Nitroanisole.—Baly, Tuck, and Marsden (*loc. cit.*) found two bands in solutions of this substance, the heads of which were at about  $1/\lambda$  3100 ( $\lambda$  3220) and  $1/\lambda$  4000 ( $\lambda$  2500) respectively.

The absorption spectrum of the vapour of the substance at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure °C. in mm.		
75	904	The rays were transmitted to $\lambda$ 2200; but they were rather weak between about $\lambda$ 2430— $\lambda$ 2350.
90	934	The rays were weakly absorbed between $\lambda$ 3050— $\lambda$ 2900; they were transmitted to about $\lambda$ 2470 and then absorbed to $\lambda$ 2330; and then transmitted to $\lambda$ 2250.
100	950	The rays were fairly well absorbed between $\lambda$ 3100— $\lambda$ 2730 although several of the strong Cd lines were visible in this region; they were then transmitted to about $\lambda$ 2550, after which there was absorption to the Cd lines 2329, 2321, and 2313 which were visible.

There were, therefore, two vapour bands which are comparable with the two solution bands, except in position. All the series of finer bands found by the authors in the vapour of anisole (T, 1912, 101, 1514) have completely disappeared.

*p*-Nitroanisole.—Solutions of this substance have not been examined, but Baly, Tuck and Marsden (*loc. cit.*) have examined *p*-nitrophenetole, and they found one band the head of which is at about  $1/\lambda$  3400 ( $\lambda$  2940).

The absorption spectrum of the vapour of *p*-nitroanisole at various

temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure in mm.		
75	904	The rays were absorbed between $\lambda$ 2900— $\lambda$ 2600 and then transmitted to $\lambda$ 2190. The Cd line 2748 was fairly well marked.
160	959	The rays were absorbed between $\lambda$ 3000— $\lambda$ 2330. The Cd lines 2329 to 2265 were well marked.

There was therefore only one large vapour band.

*o*-Nitroaniline.—Alcoholic solutions of the substance of various strengths were examined, and the curve drawn (Fig. 3, IV). There are two bands: a large, strong one in the visible part of the spectrum, the head of which is at  $1/\lambda$  2450 ( $\lambda$  4080), and a second, very weak one, the head of which is at  $1/\lambda$  3570 ( $\lambda$  2800).

The absorption spectrum of the vapour of *o*-nitroaniline at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure in mm.		
99	926	The rays were transmitted to about $\lambda$ 2420; but they were somewhat weak between $\lambda$ 3650— $\lambda$ 3350; and again between $\lambda$ 2420— $\lambda$ 2350. The series of Cd lines 2329—2194 was well marked.
100	942	The rays were very weak between $\lambda$ 3800— $\lambda$ 3500, and then transmitted to $\lambda$ 2150; the Cd lines 2329, 2321, 2313 were also easily seen.

The vapour was also examined in the less refrangible regions at the above temperatures and pressures by using the continuous spectrum of an acetylene lamp, but no fine bands were observed. The results show the presence of two bands, the more refrangible one being very faintly indicated, and there was no resolution into a series of finer bands. All the fine bands found and measured in the vapour of aniline (Purvis, *loc. cit.*) have completely disappeared.

*o*-, *m*-, and *p*-Nitrobenzaldehydes.—Alcoholic solutions of these substances were examined, and their absorption curves drawn (Fig. 3, I, II, and III). The ortho-compound shows a very weak, shallow band, the head of which is at about  $1/\lambda$  1100 ( $\lambda$  2438); it is more like a very rapid extension of the transmitted rays; the meta-compound also shows a weak, shallow band  $1/\lambda$  1110 ( $\lambda$  2430), and the para-compound shows a wide, fairly strong band at  $1/\lambda$  3800 ( $\lambda$  2630).

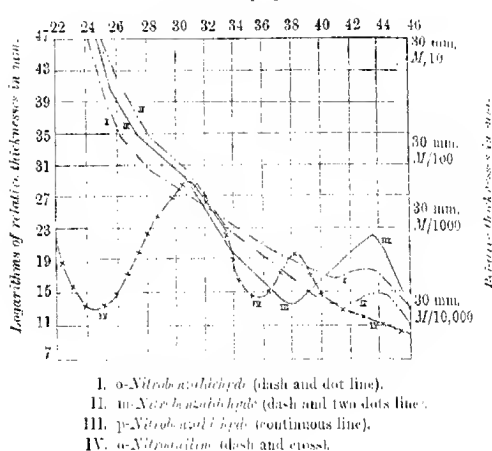
*o*-Nitrobenzaldehyde.—The absorption spectrum of the vapour of the substance at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

$t^{\circ}$	Pressure in mm.	
90	922	The rays were moderately well absorbed between about $\lambda$ 2540— $\lambda$ 2330, and then weakly transmitted to about $\lambda$ 2260.
100	938	The rays were transmitted to about $\lambda$ 2580.

There was therefore a very weak vapour band, not unlike the solution band, except that the latter is shifted more towards the red end. Also, the fine series of vapour bands, found in the vapour of benzaldehyde, have completely disappeared.

FIG. 3.

Oscillation frequencies.



*m*-Nitrobenzaldehyde.—The absorption spectrum of the vapour of the substance at various temperatures and pressures in a 200 mm tube showed the following phenomena:

$t^{\circ}$	Pressure in mm.	
75	900	The rays were transmitted to about $\lambda$ 2260; but they were a little weak between $\lambda$ 2150— $\lambda$ 2350.
100	947	The rays were transmitted to about $\lambda$ 2510.

There was therefore an exceedingly weak band, which is comparable with the very shallow solution band.

*p*-Nitrobenzaldehyde.—The absorption spectrum of the vapour

of the substance at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure		
t.	in mm.	
90	830	The rays were absorbed between $\lambda$ 2580— $\lambda$ 2321, and then weakly transmitted to about $\lambda$ 2144.
140	947	The rays were transmitted to $\lambda$ 2650, but the Cd lines 2194 and 2144 were visible.

There was therefore a fairly strong, wide band, which is comparable with the solution band, except in position.

*Nitromethane*.—Baly and Desch (T., 1908, 93, 1747) state that solutions of the substance exhibit a shallow band the head of which is at about  $1/\lambda$  3600 ( $\lambda$  2776).

The absorption spectrum of the vapour of nitromethane at various temperatures and pressures in a 200 mm. tube showed the following phenomena:

Pressure		
t.	in mm.	
45	843	The rays were transmitted to $\lambda$ 2360; but they appeared to be a little weak between about $\lambda$ 2550— $\lambda$ 2570.
60	873	The rays were transmitted to $\lambda$ 2660; but the strong Cd lines 2880, 2748, 2573 were visible.
90	843	The rays were transmitted to about $\lambda$ 3100.

There was, therefore, the doubtful appearance of a very weak vapour band which would be comparable with the shallow solution band, but there was no appearance of a series of fine bands. It will be noticed that the vapour absorbs the light very strongly at the higher temperatures and pressures.

#### *Thin Films.*

Thin films of several of the substances were also investigated by pressing tightly a small quantity of the substance between two quartz plates held in front of the slit of the spectroscope, and allowing the light of a cadmium spark to pass through for various periods of times. There was no solidification of the solids during the time of the experiment. The following phenomena were observed when the cadmium light passed through the thin films of the substances for two minutes:

<i>Phenol</i> ....	The rays were absorbed between about $\lambda$ 2850— $\lambda$ 2540 and were then transmitted to $\lambda$ 2330.
<i>o-Cresol</i> ...	The rays were absorbed between about $\lambda$ 2870— $\lambda$ 2570 and were then transmitted to $\lambda$ 2350.
<i>m-Cresol</i> ..	The rays were absorbed between $\lambda$ 2850— $\lambda$ 2580 and were then transmitted to $\lambda$ 2350.
<i>p-Cresol</i> ...	The rays were absorbed between $\lambda$ 2920— $\lambda$ 2580 and were then transmitted to $\lambda$ 2360.
<i>Catechol</i> ...	The rays were absorbed between $\lambda$ 2880— $\lambda$ 2570 and then transmitted to about $\lambda$ 2350; but the series of Cd lines from $\lambda$ 2329 to $\lambda$ 2265 were visible.
<i>Nitromethyl</i> ..	The rays were absorbed between $\lambda$ 2890— $\lambda$ 2580 and then transmitted to $\lambda$ 2400.



*Nitrobenzene*.—The absorptive power of this substance is very great. It was only by very tightly squeezing the thinnest film that the light in the regions beyond about  $\lambda$  3200 left an image on the photographic plate. After five minutes' exposure, the plate showed that the rays were transmitted very feebly to about  $\lambda$  2480; there was then absorption to the cadmium line  $\lambda$  2329, and then the series of cadmium lines to  $\lambda$  2144 were fairly well seen.

Therefore the absorption bands are similar to the solution bands. There is no appearance of any of the fine vapour bands, and the results are precisely similar to those found in all cases of thin films of the various substances in previous investigations.

Some reference should be made to the divergences noticed by Baly and Rice (T., 1913, 103, 91) in the observations of the absorption spectrum of thin films of aniline as described before (Purvis, *loc. cit.*). They suggest that the mounting of the quartz plates in the cell was not sufficiently rigid to stand the strain of the surface tension of such thin films; and that therefore the readings are much smaller than the real thickness of the film owing to the plates being forced apart by the surface tension. The authors have repeated the experiments with a film of aniline at 0.01 mm. thick, and found very similar results to what one of them found before, when using the same apparatus and the cadmium spark as the source of light. It is hardly likely that the divergences are caused by a weak rigidity of the quartz plates. Moreover, it is desirable that the exact conditions of the experimental apparatus should be stated; for example, the nature and size of the electric coil and the condenser will produce differences in the luminosity of the spark. The nature of the electrodes producing the spark, the distance of the latter from the slit, and the time of exposure will all affect the amount of light endeavouring to pass through; and in all quantitative and comparative experiments it seems to be necessary that all these conditions should be stated. With regard to the films of about 0.001 mm. thick, it was stated at the time that no great degree of exactness could be ascribed to the number. Such a thin film is difficult to obtain, for it implies plane surfaces of the quartz plates only obtainable by special methods.

#### *Discussion of the Results.*

The more important results are: (1) The large number of vapour bands in phenol quite unlike the single solution band. (2) The reduction of the number of vapour bands in catechol and guaiacol. (3) The reduction of the number of vapour bands in the cresols but not to the same extent as in the dihydroxy compounds. (4) The reduction of the number of vapour bands in the chloro-

phenols, but not to the same extent as in the cresols. (5) The reduction of the number of vapour bands in the chloroanilines when compared with those found in the vapour of aniline. (6) The reduction of the number of vapour bands in benzophenone and acetophenone when compared with the vapour of benzaldehyde. (7) The total obliteration of the finer vapour bands in the nitro-derivatives of benzene, the toluenes, the phenols, the anilines, and the aldehydes; and the similarity of the vapour bands with the solution bands, except that the latter are shifted more towards the less refrangible regions. (8) Of the isomeric substances, the ortho-compound is the most disturbed and in the meta- and para-compounds it is sometimes the former and sometimes the latter which resembles the parent substance most closely; for example, attention may be called to the cresols and the chlorophenols as illustrations.

In previous communications (Purvis, T., 1910, **97**, 692, 1035, 1546; 1911, **99**, 811, 1699, 2318) the absorption spectra of the vapours of various organic substances were discussed from the view that the fundamental vibrations were considered to be damped and dislocated by the introduction of various substituting atoms or groups of atoms; that, in solution, the tensional forces at the surfaces of the two substances restrain the oscillations still more strongly; and that the solvent also acts as an absorbent of a part of the radiant energy as well as a barrier to the mutual encounters; and that, in the thin films of the substance, the closely-packed molecules also exert a tensional effect on each other, and thereby restrict the oscillatory movements. It was also suggested that the final adjustment of the oscillations would be influenced by the mass and type of the introduced atom or atomic groups, as well as by the distribution and reaction of the vibrations consequent on the absorption of the radiant energy. For example, none of the iodine derivatives of benzene or toluene (*loc. cit.*) shows any selective absorption either as vapour or in solution or in thin films, whereas the corresponding chlorine and bromine compounds show selective absorption. It was considered that the radiant energy is primarily exerted on the movements of the molecules themselves producing general absorption; and that therefore there are no oscillations or vibrations of the atoms which could produce selective absorption in the ultra-violet regions.

In later investigations the authors (T., 1912, **101**, 1514, 1810; this vol., p. 433) have amplified these suggestions, and they submitted that selective absorption may arise from the interaction of various primary oscillation centres, such as the carbonyl group, and the ethenoid linking. In order to extend this theory further, it is

suggested that the oscillation centres are centres of electronic vibrations, set in motion by and so absorbing selectively part of the radiant energy; but the fuller development of the suggestion must be deferred until a more precise discussion can be brought forward to explain the complex phenomena in these compounds.

We desire to thank the Government Grant Committee of the Royal Society, by whose assistance a part of the cost of the research was defrayed.

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### CXVIII.—*Viscosity Maxima and Their Interpretation.*

By FERDINAND BERNARD THOLE, ALBERT GEORGE MUSSELL, and  
ALBERT ERNEST DUNSTAN.

SOME years ago (T., 1904, **85**, 817; 1905, **87**, 11) one of the present authors determined the viscosity-concentration curves of several liquid mixtures, and classified them as follows:

1. Sagged curves approximating more or less to the linear curve demanded by the law of mixtures.
2. Curves exhibiting a minimum.
3. Curves possessing a maximum.

Based on the view that associated liquids in general, and hydroxylated liquids in particular have a relatively high viscosity coefficient, the conclusion was drawn that a maximum point in a viscosity-concentration curve meant further association proceeding in the direction of complex formation, whilst the existence of a minimum point tended to the opposite view, namely, that some dissociation had resulted.

In the meantime several investigators have approached the problem, and in general the above deductions have been substantiated.

As a complete collection of viscosity curves which show a maximum point is given in the sequel, mention will only be made here very briefly of the conclusions which have been arrived at. The simple view taken by Graham (*Phil. Trans.*, 1861, **151**, 373) that the maximum point definitely indicated the existence of a compound, and, moreover, established its composition has been generally criticised as being far too explicit. It seems probable, however, that in some cases this view is sound, as will be seen later. Where, however, the amount of chemical affinity between the com-

ponents is not sufficient entirely to bring about combination, the position of the maximum will vary within limits depending on temperature, the viscosity of the constituent liquids, and the degree of dissociation of the compound.

Washburn (*Tech. Quart.*, 1908, **21**, 399), in a valuable summary of the theory of hydration, dealing with the deviations of property-composition curves from those demanded by the law of mixtures, agrees that striking irregularities exist, which may be quite invariant with temperature, such as the expansion-coefficient of aqueous solutions of nitric acid and sulphuric acid, which clearly indicate the existence of the hydrates  $\text{HNO}_3 \cdot \text{H}_2\text{O}$ ;  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . Such irregularities are not found for mixtures the components of which show no chemical affinity for each other. However, Washburn sums up his review by stating that the deviations of a physical property from the mixture law cannot give any conclusive evidence regarding the existence of a hydrate (or complex). This statement is directly contrary to the views which have been held by a great number of investigators in this field (see T., 1909, **95**, 1556).

Tsakalotos (*Bull. Soc. chim.*, 1908, [iv], **3**, 234) has also determined maximum points on viscosity-concentration curves, and holds the opinion that the study of the viscosity curves in conjunction with the freezing-point curves proves undoubtedly that the viscosity maxima must be attributed to molecular compounds in a state of partial dissociation. The discrepancy between the compositions of the mixtures of maximum viscosity and maximum freezing point for aniline-*m*-cresol, *p*-toluidine-*m*-cresol must be attributed to the difference existing between the viscosity of the two components and the partial dissociation of the molecular aggregate. He imagines the mixture as containing two different components, namely, (1) the inactive mixture of the original constituents, and (2) the complex aniline-phenol. Mixture (1) gives a linear mixture-law curve. The effect of (2) alone would be a maximum at 50 mols. per cent. The resultant of these curves has a maximum displaced towards the component of greater viscosity.

Faust (*Zeitsch. physikal. Chem.*, 1912, **95**, 1557) points out that it is very probable, although not absolutely proved, that in those cases where a maximum viscosity occurs a chemical compound is produced. Thus there is always such a maximum when the components are an acid and a base. In all cases where there is an evolution of heat on mixing, the compounds will dissociate with rising temperature, and so the viscosity curve will reproduce the dissociation by showing a smaller and smaller deviation, and at high temperatures will approach linearity. It is, however, untrustworthy to deduce from the position of the maximum the chemical com-

position of the compound, since the position frequently alters with temperature, and depends on the relative viscosities of the two components. On the other hand, when the viscosity curve is sagged, it must be interpreted as a result of dissociation (see Dunstan, T., 1904, *loc. cit.*). Faust also noticed that maxima on viscosity curves correspond with minima on vapour-pressure curves, a fact which is compatible with the formation of a molecular compound.

Denison (*Trans. Faraday Soc.*, 1912, **8**, 20) considers that the formation of a maximum does imply molecular aggregation, but prefers to determine the nature of the complex by the maximum deviation from the mixture law rather than from the position of the maximum itself. It should be mentioned that other observers have emphasised the fact that the greatest deviation should be considered, and not the actual maximum, notably Findlay (*Zritsch. physikal. Chem.*, 1909, **69**, 203). Denison assumes that where complex formation is possible, there will be a solution of the complex in a mixture of the unaltered components. This mixture of complex and unchanged components will tend to form a maximum at some point along the curve, depending on its relative viscosity. It follows as a corollary that if most or all of the components associate in this way, the maximum point must agree with the composition of the complex. As Baker (T., 1912, **101**, 1416) has indicated, however, the complex may be of less viscosity than one or other of the components (assumed to be very associated), in which case a sagged curve or a minimum might be obtained. Baker, in fact, draws the conclusion that in mixtures of alcohol-ether, used for dissolving nitrocellulose, there is a complex existing, but the shape of the curve does not in any way indicate it.

Kendall (*Medd. K. Vetensk. Nobelinst.*, 1913, **2**, No. 25), dealing with liquid mixtures of type 1, shows that the viscosity found agrees excellently with that calculated on a modified Arrhenius formula, and hence strengthens the view that in such mixtures there is little mutual action.

On surveying these various opinions, it will be evident that they conform to the belief that a maximum viscosity does indicate some molecular aggregation, but the mass of evidence is decidedly against any predication that the position of the maximum point may indicate the composition of the compound. It will be obvious that this position can be influenced by a variety of causes. Suppose two liquids, *A* and *B*, the association factors of which are *n* and *m*, tend on mixing to form the compound *AB*. Then:

$$A_n + B_m \rightleftharpoons (n-x)A + (m-x)B + xAB,$$

where *x* is the amount of *AB* present.

Four cases present themselves:

Case 1.—*x* is very small, and *A<sub>n</sub>* and *B<sub>m</sub>* are stable, and have

little mutual action. A linear or slightly sagged curve will result, for example, phenol- $\alpha$ -naphthylamine.

Case 2.  $\rightarrow x$  is fairly large, there is considerable chemical affinity, and the complexes  $A_n$  and  $B_m$  are mutually fairly stable. Then if the viscosity of the complex  $AB$  is less than that of one or other of the components, there will be a sagged curve, for example, phenol-acetone, lactic acid-water.

Case 3.  $\rightarrow x$  is fairly large, there is considerable chemical affinity, and the viscosity of the complex is greater than that of  $A_n$  and  $B_m$ , which are mutually somewhat unstable. Then there will be a maximum point, but its position will depend on temperature and the relative viscosities of  $A_n$ ,  $B_m$ , and  $AB$ , for example, alcohol-water.

Case 4.  $\rightarrow x$  is very large, and chemical action very considerable; the complexes  $A_n$  and  $B_m$  are dissociated. Then there will be a definite maximum corresponding with the actual molecular concentration of  $A$  and  $B$  in  $AB$ , for example, sulphuric acid-water.

In view of these considerations, we decided to investigate other cases of possible maximum formation, using pairs of liquids the fusion curves of which had been constructed, and we find, in brief, that in the large majority of cases a maximum in the melting-point curve means a maximum in the viscosity curve. We have found only one case as an exception to this rule, namely, acetone-phenol (Schmidlin and Lang, *Ber.*, 1910, **43**, 2812), which shows the existence of a compound at the fusion temperature, but gives only a very sagged viscosity curve. It should be mentioned also that the maximum viscosity for acetic acid water does not correspond with a maximum in the fusion curve, apparently only a eutectic point being obtained.

#### Liquid Mixtures which show Maximum Points.

Mixture.	Maximum.	Observer.	Fusion curve.
Water-methyl alcohol	al. Approximately $\text{MeOH} \cdot 3\text{H}_2\text{O}$	Gotman, Dunstan	—
Water-ethyl alcohol	al. Approximately $\text{EtOH} \cdot 3\text{H}_2\text{O}$	Poissenot, Graham, Dunstan, Traube	—
Water-propyl alcohol	al. Approximately $\text{PrOH} \cdot 2\text{H}_2\text{O}$	Dunstan	
Water-acetic acid	$\text{CH}_3\text{CO}_2\text{H} \cdot \text{H}_2\text{O}$	Graham, Dunstan, Wijkander	No maximum, Kremm, <i>Sitzungsber. K. Akad. Wiss.</i> , 1907, <b>116</b> , 795
Water-propionic acid	Approximately $\text{C}_2\text{H}_5\text{CO}_2\text{H} \cdot \text{H}_2\text{O}$	Taskalotos	
Water-pyridine	Approximately $2\text{C}_5\text{H}_5\text{N} \cdot 5\text{H}_2\text{O}$	Hartley, Thomas and Appleby	
	Approximately 30 vols. per cent. pyridine	Dunstan and Fausst	

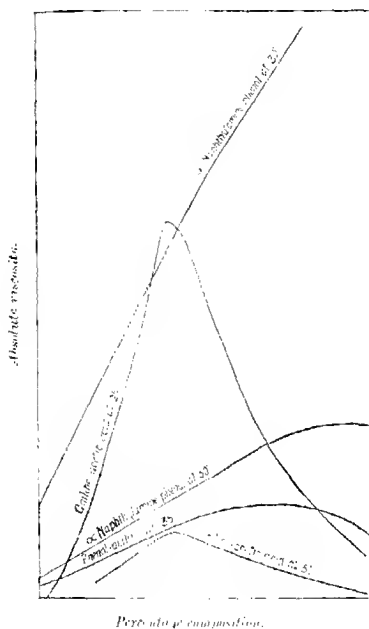
*Liquid Mixtures which show Maximum Points* (continued).

Mixture.	Maximum.	Observer.	Fusion curve.
Water-sulphuric acid	$\text{H}_2\text{SO}_4\text{H}_2\text{O}$	Graham, Knietzsch, Dunstan	Maximum, $\text{H}_2\text{SO}_4\text{H}_2\text{O}$ .
Sulphuric acid-sulphur trioxide	$\text{H}_2\text{SO}_4\text{SO}_3$	Dunstan and Wilson	Knietzsch, Kramann, Knietzsch, maximum
Aniline- <i>m</i> -cresol	Approximately 2 <i>m</i> -cresol : 1 aniline	Tsakalotos	Maximum, Kramann, <i>Sitzungsber. K. Akad. Wien</i> , 1905, 112, 1201. Kramann, <i>loc. cit.</i>
<i>o</i> -Toluidine- <i>m</i> -cresol	Approximately 4 <i>m</i> -cresol : 1 toluidine	Tsakalotos	
Acetone-chloroform.	Approximately 4 chloroform : 1 acetone at 0° and 3 chloroform Faust : 1 acetone at 13°	Tsakalotos	
Pyridine-acetic acid	No maximum at 19° Faust Approximately 4 acetic acid : 1 pyridine Approximately 4 acetic acid : 1 pyridine Very slight shift of Faust maximum between 0° and 99°	Tsakalotos	
Pyridine-butyric acid	Approximately 4 butyric acid : 1 pyridine	Tsakalotos	
Aniline-acetic acid.	Approximately 2 acetic acid : 1 aniline at 18°—60°	Faust	
Acetic anhydride-water	Approximately 2 water : 1 anhydride, invariant between 0° and 73°	Faust	
<i>iso</i> Butyric acid-water	Approximately 3 water : 1 acid	Tsakalotos	
<i>n</i> -Butyric acid-water	Approximately 2 water : 1 acid	Tsakalotos	
Triethylamine-water	Approximately 5 water : 1 amine	Tsakalotos	
Nicotine-water	Approximately 3 water : 1 amine	Tsakalotos	
Allylthiocarbamide-piperidine	Exactly 1 amine : 1 thiocarbamide	Kurnakov and Schentschinski, <i>J. Russ. Phys. Chem. Soc.</i> , 1912, 44, 1964	
Phenylthiocarbimide-diethylamine	Exactly 1 amine : 1 thiocarbimide	"	
Allylthiocarbimide-methylaniline	Exactly 1 amine : 1 thiocarbimide	"	
Ethylthiocarbimide-piperidine	Exactly 1 amine : 1 thiocarbimide	"	

## EXPERIMENTAL.

We have examined the following liquid pairs: Aniline-acetic acid, *o*-chlorophenol-aniline, *p*-chlorophenol-aniline, *m*-chlorophenol-aniline, phenol-phenylhydrazine, *o*-chlorophenol-phenylhydrazine, *p*-cresol-aniline, *p*-toluidine-phenol,  $\alpha$ -naphthylamine-phenol,

FIG. 1.



aniline-phenol, *o*-nitrophenol-*p*-toluidine, and phenol-diphenylamine.

The materials used were obtained from Schuchardt, and carefully purified by appropriate means. The apparatus used has been fully described in the past, but mention may be made of the new type of Ostwald viscometer described recently by one of us (Thole, this vol., p. 22), which seems absolutely free from the drawbacks inherent to the vertical type. In several cases we have determined



the viscosity at two temperatures to decide whether an appreciable drift of maximum does occur. It may be said at once that where there is any considerable amount of affinity between the components no such drift is noticeable.

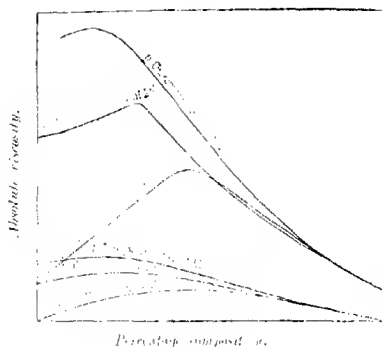
### 1. Aniline-Acetic Acid. (Fig. 1.)

Aniline, Per cent.	$d_{20}^4$	$\eta_{25}$	$d_{50}^4$	$\eta_{50}$
0.0	1.052	0.0134	—	—
15.5	1.082	0.0729	1.047	0.0296
24.7	1.091	0.123	—	—
37.9	1.088	0.219	1.056	0.0565
40.9	1.085	0.214	1.057	0.0558
44.5	1.084	0.203	1.051	0.0527
49.55	1.076	0.181	—	—
62.3	1.061	0.118	1.035	0.0382
100.0	1.022	0.0362	0.992	0.0201

Maximum at 25°, 40 per cent. aniline; at 50°, 39 per cent.

$\text{C}_6\text{H}_5\text{NH}_2\text{CH}_3\text{CO}_2\text{H}$  requires 61 per cent. aniline.

FIG. 2.



### 2. Aniline o-Chlorophenol. (Fig. 2.)

Aniline, Per cent.	$d_{20}^4$	$\eta_{25}$	$d_{50}^4$	$\eta_{50}$
0.0	1.225	0.0111	1.203	0.02015
8.1	1.216	0.0538	1.184	0.0257
15.0	1.199	0.0671	1.168	0.0288
19.1	1.146	0.0951	1.118	0.0430
41.8	1.142	0.0963	1.111	0.0335
49.65	1.131	0.0944	1.105	0.0326
57.4	1.091	0.0771	1.072	0.0304
77.3	1.059	0.0649	1.055	0.0277
100.0	1.022	0.0362	0.992	0.0201

Maximum at 25°, 45 per cent. aniline. Maximum at 50°, 41 per cent. aniline.

$\text{C}_6\text{H}_5\text{NH}_2\text{C}_6\text{H}_4\text{ClOH}$  requires 42 per cent. aniline.

3. *Aniline-m-Chlorophenol.* (Fig. 2.)

Aniline, Per cent.	$d_{20}^0$	$\eta_{20}$	$d_{20}^0$	$\eta_{20}$
0.0	1.268	0.1155	1.237	0.0398
9.0	1.238	0.1185	1.210	0.01135
19.35	1.207	0.1246	1.180	0.0434
29.1	1.181	0.1322	1.153	0.0449
40.3	1.153	0.1083	1.126	0.0403
60.1	1.104	0.0811	1.077	0.0321
75.4	1.071	0.0613	1.045	0.0265
100.0	1.022	0.0362	0.992	0.0210

Maximum at 25°, 29 per cent. Maximum at 50°, 29 per cent.

$C_6H_5 \cdot NH_2 \cdot C_6H_4Cl \cdot OH$  requires 42 per cent. aniline.

4. *Aniline p-Chlorophenol.* (Fig. 2.)

Aniline, Per cent.	$d_{20}^0$	$\eta_{20}$	$d_{20}^0$	$\eta_{20}$
0.0	—	—	1.244	0.0499
7.8	1.249	0.168	1.223	0.0514
15.4	1.228	0.172	1.199	0.0537
22.2	1.209	0.171	1.179	0.0537
29.0	1.185	0.157	1.158	0.0513
37.2	1.166	0.141	1.140	0.0480
41.8	1.154	0.131	1.125	0.0451
50.2	1.133	0.112	1.107	0.0419
70.2	1.084	0.0705	1.058	0.0307
90.3	1.037	0.0452	1.012	0.0221
100.0	1.022	0.0362	0.992	0.0201

Maximum at 20 per cent. aniline. Maximum at 20 per cent. aniline.

$C_6H_5 \cdot NH_2 \cdot C_6H_4Cl \cdot OH$  requires 42 per cent. aniline.

5. *Phenylhydrazine Phenol.* (Fig. 3.)

Maximum in fusion curve at equimolecular proportions (Ciussa and Bernardi, *Gazzetta*, 1910, 40, i, 159).

Phenyl hydrazine, Per cent.	$d_{20}^0$	$\eta_{20}$	Phenyl hydrazine, Per cent.	$d_{20}^0$	$\eta_{20}$
0.0	1.048	0.0329	53.7	1.069	0.0820
20.2	1.056	0.0625	62.8	1.069	0.0805
40.2	1.065	0.07485	80.4	1.069	0.06555
50.2	1.068	0.0822	100.0	1.068	0.0458

Maximum at 54 per cent. phenylhydrazine.

$NHPh \cdot NH_2 \cdot Ph \cdot OH$  requires 53 per cent. phenylhydrazine.

6. *Phenylhydrazine m-Chlorophenol.* (Fig. 3.)

Phenyl hydrazine, Per cent.	$d_{20}^0$	$\eta_{20}$	Phenyl hydrazine, Per cent.	$d_{20}^0$	$\eta_{20}$
0.0	1.203	0.02015	49.3	1.145	0.0818
14.75	1.187	0.0354	75.0	1.108	0.06755
35.0	1.166	0.0716	100.0	1.068	0.0458
46.5	1.154	0.0827			

Maximum at 46 per cent. phenylhydrazine.

$NHPh \cdot NH_2 \cdot C_6H_4Cl \cdot OH$  requires 46 per cent. phenylhydrazine.

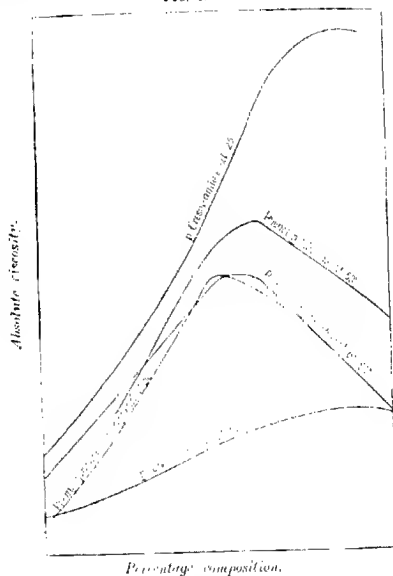
7. *p*-Cresol-Aniline. (Fig. 3.)

<i>p</i> -Cresol. Per cent.	$d_{20}$	$\eta_{sp}$	$d_{20}$	$\eta_{sp}$
0.0	1.020	0.0362	0.992	0.0201
30.0	1.022	0.0695	0.997	0.0293
53.6	1.027	0.107	1.001	0.03975
62.7	1.028	0.121	1.004	0.0426
79.5	1.028	0.144	1.005	0.0462
90.0	1.029	0.145	1.005	0.0471
100.0	—	—	1.005	0.0462

Maximum at 25°, 86 per cent. *p*-cresol.      Maximum at 50°, 90 per cent. *p*-cresol.

Maximum on fusion curve at equimolecular proportions (Phillips, T., 1903, 83, 814).

FIG. 3.

8. Phenol-*p*-Toluidine. (Fig. 3.)

Phenol. Per cent.	$d_{20}$	$\eta_{sp}$	Phenol. Per cent.	$d_{20}$	$\eta_{sp}$
0.0	—	—	62.2	1.0375	0.092
39.9	1.016	0.0757	71.5	1.043	0.0984
47.5	1.021	0.0864	100.0	1.067	0.0700
58.8	1.032	0.0942			

Maximum at 63 per cent. phenol.

$\text{PhOH} \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$  requires 48 per cent. phenol.

Maximum on fusion curve at equimolecular proportions (Phillips,

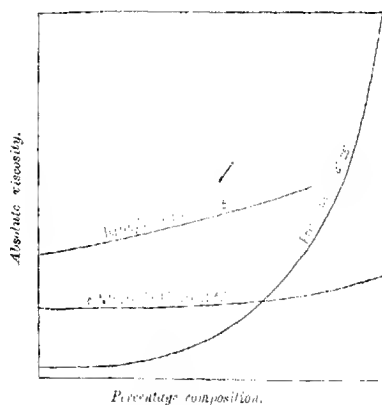
9.  $\alpha$ -Naphthylamine-Phenol. (Fig. 1.)

$\alpha$ -Naphthylamine. Per cent.	$d_{20}$ .	$\eta_{sp}$ .	$d_{20}$ .	$\eta_{sp}$ .
0.0	1.067	0.0700	1.048	0.0320
52.0	1.094	0.249	1.075	0.0852
56.5	1.097	0.269	1.076	0.0960
79.1	1.106	0.324	1.092	0.109
92.5	—	—	1.102	0.113
100.0	—	—	1.108	0.112

 Maximum at 50°, 92 per cent.  $\alpha$ -naphthylamine.

Maximum on fusion curve at equimolecular proportions (Philip).

FIG. 4.



## 10. Aniline-Phenol. (Fig. 1.)

Phenol. Per cent.	$d_{20}$ .	$\eta_{sp}$ .	Phenol. Per cent.	$d_{20}$ .	$\eta_{sp}$ .
0.0	1.007	0.0279	67.9	1.049	0.0721
35.1	1.030	0.0539	79.7	1.055	0.0992
51.4	1.040	0.0654	100.0	—	0.0555

Maximum at 70 per cent. phenol.

 Maximum on fusion curve at equimolecular proportions (Schreinemakers, *Zeitsch. physikal. Chem.*, 1899, **31**, 581).

## 11. Diphenylamine-Phenol. (Fig. 4.)

Diphenylamine. Per cent.	$d_{20}$ .	$\eta_{sp}$ .
0.0	1.048	0.0320
32.4	1.048	0.03825
58.9	1.052	0.04362
79.5	1.055	0.0501
100.0	—	—

A very slightly sagged curve. Philip showed (*loc. cit.*) that the fusion curve only exhibits a eutectic point.

12. *o*-Nitrophenol-*p*-Toluidine. (Fig. 4.)

<i>o</i> -Nitrophenol. Per cent.	$d_{20}^{\circ}$	$\eta_{20}^{\circ}$
0.0	0.953	0.0139
35.3	1.050	0.01835
79.6	1.220	0.0215
100.0	1.282	0.0268

A distinctly sagged curve. Philip showed also that this system merely gave a eutectic point.

It will be noticed from the above tables that in some cases the evidence of the fusion curves is closely paralleled by that of the viscosity curves, for example, for sulphuric acid-water, *o*-chlorophenol-aniline, phenol-phenylhydrazine, aniline-phenol, *o*-chlorophenol-phenylhydrazine. In the majority of maxima, however, there is a distinct shift from the point of equimolecular concentration. We therefore incline to the view that the appearance of a maximum on a viscosity concentration curve does indicate the existence of chemical combination between the components, but the position depends on several independent factors, namely, the actual viscosity of the components (which is intimately connected with their degree of association), and the degree of dissociation of the compound itself at the temperature of observation. It by no means follows that the absence of a maximum point precludes complex formation, as, indeed, has been pointed out by one of us repeatedly, for obviously the viscosity of one highly associated component may be greater than that of the complex (see also Baker, *loc. cit.*). Comparison of the viscosity with the fusion curves and with the vapour pressure curves is valuable, for, as Faust has indicated, there is a close connexion between vapour pressure and viscosity, since whatever forces operate in complex building would similarly depress vapour tension. In an attempt to test these views experimentally, we first determined the viscosity of two pairs, which gave only eutectic points on their fusion curves, namely, phenol-diphenylamine, and *o*-toluidine-*o*-nitrophenol (Philip, *loc. cit.*). We obtained a linear density curve and sagged viscosity curves (Fig. 4), which evidently confirms the view that little or no complex formation is proceeding, or else that the compound had a smaller viscosity than the components, but seeing that *o*-nitrophenol is very slightly associated (Thole, T., 1910, 97, 2596), and its viscosity is depressed by adding phenol, it is obvious that no compound formation is going on. This is a case where Denison would probably suggest that the

maximum sag was due to the appearance of a compound. Similar remarks may be made about the phenol-diphenylamine curve, which is almost linear.

It can therefore safely be predicted that wherever the two components show little tendency for chemical union a sagged curve, or one departing but slightly from linearity, will be found.

A very striking confirmation of the validity of these views has just appeared in a paper by Kurnakov and Schemtschushni (*loc. cit.*). These authors have investigated at various temperatures the viscosity concentration curves of irreversible binary systems where liquid and completely miscible compounds are formed. The viscosity isotherms consist of two separate branches convex to the composition axis intersecting at an angle (increasing in acuteness as the temperature is lowered), and this maximum point is invariant at exactly equimolecular concentration. This condition of affairs was predicted in Case 4.

The authors desire to thank the Research Fund Committee of the Chemical Society for grants in aid of this work.

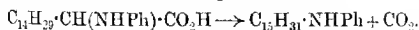
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### CXIX.—*Preparation of Secondary Amines from Carboxylic Acids. Part III. Dissecondary Amines from Dicarboxylic Acids.*

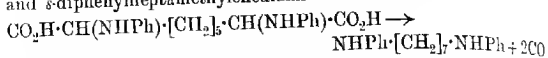
By HENRY RONDEL LE SUEUR.

THE first and second parts of this investigation (T., 1910, **97**, 2433; 1911, **99**, 827) dealt with the preparation of the higher alkyl derivatives of aniline and  $\alpha$ - and  $\beta$ -naphthylamine by the action of heat on the corresponding  $\alpha$ -anilino- and  $\alpha$ -naphthylamino-acids. Thus it was shown that a 70 per cent. yield of pentadecylaniline is readily obtained from  $\alpha$ -anilinopalmitic acid:

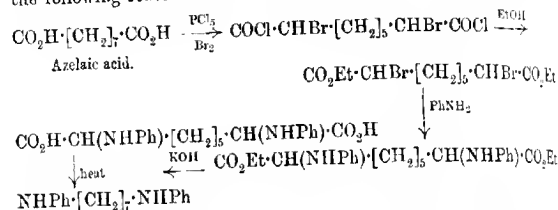


The present communication deals with the results of a similar investigation of the  $\alpha$ -anilino- and  $\alpha$ -1- and 2-naphthylamino-derivatives of dicarboxylic acids, and the results obtained show that the decomposition by heat of these substituted dicarboxylic acids is in every way similar to that undergone by the analogous derivatives of monocarboxylic acids. Thus,  $\alpha$ -dianilinooazelaic acid,

when heated above its melting point, readily loses carbon dioxide, and *s*-diphenylheptamethylenediamine results:



The preparation of the dianilino- and dinaphthylamino-acids presents no great difficulty, and the yield of amino is generally a very satisfactory one. Thus, 19 grams of pure *s*-diphenylheptamethylenediamine were obtained from 33 grams of azelaic acid by the following reactions:

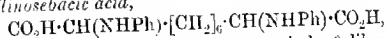


It is obvious that there is no possibility of the formation of tertiary amines by the decomposition of these  $\alpha$ -substituted acids, and this circumstance renders the method now described for the preparation of secondary amines preferable to the one commonly employed, that is, the action of an alkyl iodide on a primary amine. Further acids are more easily obtained than any other class of organic compounds, whereas monoalkyl iodides, especially the higher ones, are, as a rule, difficult to prepare.

#### EXPERIMENTAL.

*Diphenyloctamethylenediamine*,  $\text{NPh}\cdot[\text{CH}_2]_8\cdot\text{NPh}$ .

*$\alpha\delta$ -Dianilinoazelaic acid*,



was prepared by the action of aniline on ethyl  $\alpha\beta$ -dibromosebacate and subsequent hydrolysis of the anilino-ester, as described in a former communication (T., 1910, 97, 180). The finely powdered dianilinoazelaic acid, in quantities of 10 grams, was placed in a small distillation flask, which was connected to a second distillation flask, and the latter joined to a pump. When the pressure had fallen to 25–30 mm., the acid was carefully heated until it was melted, and on raising the temperature further, carbon dioxide was readily given off. The evolution of gas is liable to become unduly rapid if the heating is effected too rapidly. When no more gas was evolved, the temperature was raised further, and the product slowly distilled. The distillate, which weighed 5.7 grams

and readily solidified on cooling, was spread on porous plate and crystallised from light petroleum. The yield of pure amine was 69 per cent. of the theoretical:

0.1566 gave 0.4500  $\text{CO}_2$  and 0.1264  $\text{H}_2\text{O}$ .  $\text{C}=81.49$ ;  $\text{H}=9.33$ .

0.1278 „ 10.6 c.c.  $\text{N}_2$  (moist) at  $19.5^\circ$  and 760 mm.  $\text{N}=9.49$ .

$\text{C}_{24}\text{H}_{28}\text{N}_2$  requires  $\text{C}=81.08$ ;  $\text{H}=9.45$ ;  $\text{N}=9.45$  per cent.

*Bisphenyloctamethylenediamine* is readily soluble in ether, chloroform, benzene, or acetone, but sparingly so in cold alcohol or light petroleum, and crystallises from the latter solvent in stellar groups of stout needles, melting at  $61^\circ$ . When treated with nitrous acid, it yields a product which gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*,  $\text{NPh}[\text{CH}_2]_8\text{NPh}\cdot 2\text{HCl}$ , was readily obtained as a crystalline precipitate by adding concentrated hydrochloric acid to a warm alcoholic solution of the amine, and was purified by crystallisation from alcohol containing a little hydrochloric acid. It is insoluble in the common organic solvents except alcohol, in which it is sparingly soluble. It melts and decomposes at about  $258^\circ$ :

0.1413 gave 9.4 c.c.  $\text{N}_2$  (moist) at  $13^\circ$  and 758 mm.  $\text{N}=7.84$ .

$\text{C}_{24}\text{H}_{28}\text{N}_2\cdot 2\text{HCl}$  requires  $\text{N}=7.58$  per cent.

*Bisacetylphenyloctamethylenediamine*,  $\text{NPhAc}[\text{CH}_2]_8\text{NPhAc}$ , was prepared by boiling the base with an excess of acetic anhydride, and was purified by crystallisation from light petroleum, from which it separates in thin, glistening plates, melting at  $86\text{--}87^\circ$ . The compound dissolves readily in the common organic solvents except light petroleum, in which it is sparingly soluble:

0.1318 gave 8.3 c.c.  $\text{N}_2$  (moist) at  $16.5^\circ$  and 768 mm.  $\text{N}=7.40$ .

$\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_2$  requires  $\text{N}=7.37$  per cent.

The *benzenesulphonyl* derivative,  $\text{SO}_2\text{Ph}\cdot\text{NPh}[\text{CH}_2]_8\text{NPh}\cdot\text{SO}_2\text{Ph}$ , was prepared by heating in boiling water for five hours a mixture of half a gram of the base and 2 grams of benzenesulphonyl chloride dissolved in 10 grams of dry pyridine. The resulting solution was poured on crushed ice, and the solid collected, dried, and crystallised from alcohol:

0.1852 gave 8.5 c.c.  $\text{N}_2$  (moist) at  $15^\circ$  and 766 mm.  $\text{N}=5.40$ .

$\text{C}_{32}\text{H}_{36}\text{O}_4\text{N}_2\text{S}_2$  requires  $\text{N}=4.90$  per cent.

*Bisbenzenesulphonyldiphenyloctamethylenediamine* is insoluble in ether or light petroleum, dissolves readily in benzene, chloroform, or acetone, and crystallises from alcohol in needles melting at  $121\text{--}122^\circ$ .



*Preparation of  $\alpha\theta$ -Di-2-naphthylaminosebacic Acid,*  
 $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}\cdot\text{C}_{10}\text{H}_7)\cdot[\text{CH}_2]_6\cdot\text{CH}(\text{NH}\cdot\text{C}_{10}\text{H}_7)\cdot\text{CO}_2\text{H}.$

Ten grams of ethyl  $\alpha\theta$ -dibromosebacate and 17 grams of  $\beta$ -naphthylamine were heated together for nine hours in a flask immersed in boiling water. The product was first repeatedly digested with hot dilute hydrochloric acid, and then crystallised from a mixture of alcohol and ethyl acetate, from which it separates in crystalline nodules, melting at 132—134°:

0.2426 gave 11.2 c.c.  $\text{N}_2$  (moist) at 14° and 754 mm.  $\text{N} = 5.39$ ,  
 $\text{C}_{34}\text{H}_{40}\text{O}_4\text{N}_2$  requires  $\text{N} = 5.19$  per cent.

*Ethyl  $\alpha\theta$ -di-2-naphthylaminosebacate,*

$\text{CO}_2\text{Et}\cdot\text{CH}(\text{NH}\cdot\text{C}_{10}\text{H}_7)\cdot[\text{CH}_2]_6\cdot\text{CH}(\text{NH}\cdot\text{C}_{10}\text{H}_7)\cdot\text{CO}_2\text{Et}$ ,  
 is insoluble in ether or light petroleum, is sparingly so in boiling alcohol or ethyl acetate, and readily soluble in cold chloroform. The hydrolysis of the above ester was effected by boiling it with an excess of 10 per cent. alcoholic solution of potassium hydroxide. The resulting solution was poured into excess of hot dilute hydrochloric acid, and the precipitated acid collected, well washed, and dried. Owing to the insolubility of this naphthylamino-acid, no suitable solvent could be found for its purification by crystallisation, consequently it was twice dissolved in a dilute solution of potassium hydroxide and reprecipitated by dilute hydrochloric acid, filtered, well washed, and dried.

$\alpha\theta$ -Di-2-naphthylaminosebacic acid is insoluble in water and all the common organic solvents; it melts with decomposition and evolution of gas at 222—227°:

0.2274 gave 11.5 c.c.  $\text{N}_2$  (moist) at 16° and 758 mm.  $\text{N} = 5.88$ ,  
 $\text{C}_{30}\text{H}_{32}\text{O}_4\text{N}_2$  requires  $\text{N} = 5.79$  per cent.

*s-Di-2-naphthyl-octamethylenediamine,  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot[\text{CH}_2]_8\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ .*

$\alpha\theta$ -Di-2-naphthylaminosebacic acid in quantities of 10 grams was heated under a pressure of 30 mm., as described for the preparation of diphenyloctamethylenediamine (p. 1120), and when the evolution of carbon dioxide had ceased, the temperature was raised, and the product slowly distilled at 20 mm. pressure. The semi-solid distillate was spread on porous plate, and the solid crystallised from a mixture of alcohol and light petroleum. The isolation of the base is difficult, and this no doubt accounts in some measure for the low yield (15 per cent.) of pure base obtained:

0.1636 gave 10.0 c.c.  $\text{N}_2$  (moist) at 13° and 746 mm.  $\text{N} = 7.09$ ,  
 $\text{C}_{38}\text{H}_{32}\text{N}_2$  requires  $\text{N} = 7.07$  per cent.

*s-Di-2-naphthyl-octamethylenediamine* is readily soluble in chloro-

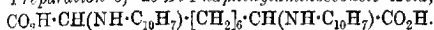
form or benzene, sparingly so in ether or alcohol in the cold, and separates from the latter solvent in small, lens-shaped crystals, melting at 100°. The product obtained by treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The hydrochloride,  $C_{10}H_7 \cdot NH \cdot [CH_2]_6 \cdot NH \cdot C_{10}H_7 \cdot 2HCl$ , was obtained as a crystalline precipitate by passing dry hydrogen chloride through a solution of the base in benzene, and was purified by crystallisation from methyl alcohol, in which it is sparingly soluble. It melts and decomposes at 244°:

0.1516 gave 7.7 c.c.  $N_2$  (moist) at 14° and 760 mm.  $N=5.97$ .

$C_{28}H_{32}N_2 \cdot 2HCl$  requires  $N=5.97$  per cent.

*Preparation of  $\alpha\beta$ -Di-1-naphthylaminosebacic Acid,*

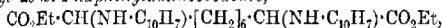


Forty grams of ethyl  $\alpha\beta$ -dibromosebacate and 68 grams of  $\alpha$ -naphthylamine were heated together in a flask immersed in boiling water for fourteen hours, and the product worked up, as described for the preparation of the corresponding  $\beta$ -naphthylamino-compound (p. 1122):

0.2228 gave 10.2 c.c.  $N_2$  (moist) at 17° and 748 mm.  $N=5.23$ .

$C_{34}H_{40}O_4N_2$  requires  $N=5.19$  per cent.

*Ethyl  $\alpha\beta$ -Di-1-naphthylaminosebacate,*



is insoluble in ether or light petroleum in the cold, dissolves readily in benzene, acetone, or chloroform, and separates from its solution in alcohol in crystalline nodules, melting at 117—119°.

$\alpha\beta$ -Di-1-naphthylaminosebacic acid was obtained by hydrolysis of the above ester as described for the preparation of the corresponding 2-naphthylamino-acid. As the acid separates with difficulty from its solutions in organic solvents, it was purified by repeated solution in dilute potassium hydroxide and reprecipitation by acid. It is insoluble in light petroleum, but dissolves readily in alcohol, acetone, chloroform, or benzene, and separates slowly from its concentrated solution in ethyl acetate in small, crystalline nodules, which melt and decompose at about 180°:

0.2230 gave 10.2 c.c.  $N_2$  (moist) at 13° and 770 mm.  $N=5.48$ .

$C_{30}H_{32}O_4N_2$  requires  $N=5.78$  per cent.

*$\delta\delta$ -Di-1-naphthyl-octamethylenediamine,  $C_{10}H_7 \cdot NH \cdot [CH_2]_8 \cdot NH \cdot C_{10}H_7$ .*

$\alpha\beta$ -Di-1-naphthylaminosebacic acid in quantities of 5 grams was heated, and the products distilled as described for the preparation of di-2-naphthyl-octamethylenediamine (p. 1122). The alcoholic

solution of the distillate slowly deposited well-formed prisms of the base, which were separated, and crystallised from methyl alcohol:

0.1060 gave 0.6 c.c.  $N_2$  (moist) at  $22^\circ$  and 766 mm.  $N = 7.11$ .

$C_{28}H_{32}N_2$  requires  $N = 7.07$  per cent.

*s*-Di-1-naphthyl-octamethylenediamine is readily soluble in ether, benzene, or chloroform, sparingly so in ethyl or methyl alcohol, and crystallises from the latter solvent in stellar groups of stout needles, melting at  $91-92^\circ$ . The product obtained by treating the base with nitrous acid gives Liebermann's reaction for nitrosoamines.

The yield of pure amine was less than that of the corresponding  $\beta$ -naphthyl derivative, and the explanation given to account for the low yield of the latter applies even more so in the case of the former, since derivatives of  $\alpha$ -naphthylamine are generally more difficult to crystallise than the  $\beta$ -naphthylamine compounds.

*Ethyl  $\alpha$ -Dibromoazelaate*,  $CO_2Et \cdot CHBr \cdot [CH_2]_5 \cdot CHBr \cdot CO_2Et$ .

Twenty grams of pure azelaic acid (m. p.  $105^\circ$ ) were treated with 45 grams of phosphorus pentachloride, and 39 grams of bromine slowly added to the resulting acid chloride. The mixture was carefully heated on the water-bath, and when all the bromine had disappeared, the bromo-acid chloride was poured slowly into 100 c.c. of alcohol. The alcoholic solution, after remaining overnight, was heated on the water-bath for half-an-hour, then cooled and poured into a large volume of water, and the ester extracted with ether. The ethereal solution was dried, evaporated, and the residue fractionally distilled under diminished pressure.

*Ethyl  $\alpha$ -Dibromoazelaate* is a colourless, oily liquid, boiling at  $238^\circ/30$  mm.:

0.2436 gave 0.2234 AgBr. Br = 39.1.

$C_{13}H_{22}O_4Br_2$  requires Br = 39.8 per cent.

*$\alpha$ -Dianilinoazelaic Acid*,  
 $CO_2H \cdot CH(NHPh) \cdot [CH_2]_5 \cdot CH(NHPh) \cdot CO_2H$ .

Twenty-five grams of ethyl  $\alpha$ -dibromoazelaate and 28 grams of recently distilled aniline were heated together in a flask immersed in boiling water for nine hours. The product was poured into excess of dilute potassium hydroxide, and the precipitated anilino-ester and aniline extracted with ether. The ethereal solution was washed, dried, and the residue left on evaporation of the ether was heated at  $230^\circ/90$  mm. in order to remove the excess of aniline. The undistilled residue, consisting of anilino-ester, was hydrolysed by boiling with a 25 per cent. alcoholic solution of potassium hydroxide, and when the hydrolysis was complete the

solution was diluted with water, the alcohol removed by evaporation, and the anilino-acid precipitated by the addition of dilute hydrochloric acid. Care must be taken not to add any large excess of mineral acid, otherwise the anilino-acid will be redissolved. The precipitated acid was collected, dried, and crystallised from alcohol, when it was obtained in small, crystalline nodules, melting at  $192-194^{\circ}$ . It is insoluble in light petroleum, ethyl acetate, or acetone in the cold, sparingly so in boiling alcohol, and dissolves readily in dilute hydrochloric acid:

0.1550 gave 10.2 c.c.  $N_2$  (moist) at  $15^{\circ}$  and 762 mm.  $N=7.72$ .

$C_{21}H_{26}O_4N_2$  requires  $N=7.57$  per cent.

0.1906, dissolved in alcohol, required 10.0 c.c.  $N/10$ -NaOH for neutralisation, using phenolphthalein as indicator, whereas the same amount of the dibasic acid,  $C_{21}H_{26}O_4N_2$ , requires 10.3 c.c.  $N/10$ -NaOH.

*s*-Diphenylheptamethylenediamine,  $NHPh\cdot[CH_2]_7\cdot NHPh$ .

$\alpha_7$ -Dianilinoazelaic acid was heated in quantities of not more than 25 grams and under 20 mm. pressure, as described for the preparation of diphenyloctamethylenediamine (p. 1120), and when the evolution of carbon dioxide had ceased, the product was distilled slowly. The distillate readily solidified on cooling, and was crystallised from a mixture of methyl alcohol and ether, from which the amine separates out in thin plates, melting at  $51-52^{\circ}$ :

0.1616 gave 0.4760  $CO_2$  and 0.1322  $H_2O$ .  $C=80.34$ ;  $H=9.09$ .

0.1460 „ 12.3 c.c.  $N_2$  (moist) at  $17^{\circ}$  and 766 mm.  $N=9.86$ .

$C_{19}H_{25}N_2$  requires  $C=80.85$ ;  $H=9.22$ ;  $N=9.93$  per cent.

*s*-Diphenylheptamethylenediamine is readily soluble in dilute hydrochloric acid and the common organic solvents except light petroleum and methyl alcohol. The product obtained by treating the base with nitrous acid gives Liebermann's reaction for nitrosoamines.

The decomposition of the anilinoazelaic acid into diphenylheptamethylenediamine and carbon dioxide takes place quite smoothly, and the yield of base is very satisfactory (see introduction, p. 1120).

The hydrochloride,  $NHPh\cdot[CH_2]_7\cdot NHPh\cdot 2HCl$ , was readily obtained by dissolving the base in warm hydrochloric acid and evaporating the solution in a vacuum. It was purified by crystallisation from a mixture of alcohol and ether, from which it separates out in stellar groups of needles, melting at  $193-194^{\circ}$ . It is insoluble in the common organic solvents with the exception of hot alcohol, in which it dissolves readily. Its aqueous solution is strongly acid to litmus:

0.1750 gave 11.4 c.c.  $N_2$  (moist) at  $18^\circ$  and 771 mm.  $N=7.63$ ,  
 $C_{19}H_{26}N_2 \cdot 2HCl$  requires  $N=7.88$  per cent.

The *acetyl* derivative,  $NPhAc \cdot [CH_2]_7 \cdot NPhAc$ , was obtained by boiling for one hour on the water-bath a mixture of 1 gram of the base and 2 grams each of acetyl chloride and acetic anhydride. The excess of the two reagents was removed by allowing the product to remain over a concentrated solution of potassium hydroxide in a vacuum, and the residue crystallised from light petroleum:

0.1710 gave 11.6 c.c.  $N_2$  (moist) at  $19.5^\circ$  and 764 mm.  $N=7.82$ ,  
 $C_{23}H_{30}O_2N_2$  requires  $N=7.65$  per cent.

*s*-Diacetyldiphenylheptamethylenediamine is readily soluble in alcohol, benzene, or chloroform, moderately so in boiling ether or light petroleum, and separates from the latter solvent in clusters of stout needles, melting at  $79-80^\circ$ .

The *benzenesulphonyl* derivative,  $SO_2Ph \cdot NPh \cdot [CH_2]_7 \cdot NPh \cdot SO_2Ph$ , was prepared by heating for five hours in boiling water a mixture of 1.5 grams of the base and 4 grams of benzenesulphonyl chloride dissolved in 14 c.c. of dry pyridine. The resulting solution was poured on crushed ice, the precipitated solid dissolved in ether, and the ethereal solution washed with dilute hydrochloric acid and water and dried. The residue left on evaporation of the ether was crystallised from alcohol:

0.1846 gave 8.4 c.c.  $N_2$  (moist) at  $15^\circ$  and 766 mm.  $N=5.37$ ,  
 $C_{31}H_{31}O_4N_2S_2$  requires  $N=4.98$  per cent.

*s*-Dibenzene sulphonyldiphenylheptamethylenediamine is readily soluble in chloroform, benzene, or acetone, and crystallises from alcohol in stout prisms, melting at  $96-97^\circ$ .

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## VAN'T HOFF MEMORIAL LECTURE.

DELIVERED ON MAY 22ND, 1913,

BY JAMES WALKER, D.Sc., Ph.D., LL.D., F.R.S.

THE work of van't Hoff is indissolubly woven in the texture of the chemistry of to-day. Whether we are organic chemists, inorganic chemists, or physical chemists, we constantly utilise and apply his ideas, reap the benefit of the intense thought he devoted to the fundamental problems of our science. This is his splendid and enduring memorial. Nothing can add to it, nothing detract from it. Feeling this profoundly, I conceive that I may best discharge the honourable responsibility laid upon me by the Society if I give a sketch of his life, his main achievements, and his way of thinking with as little discussion and elaboration as possible, and as simply as I may.\*

Jacobus Henricus van't Hoff was born in Rotterdam on the 30th of August, 1852. He came of pure Dutch stock, and his ancestry can be traced back to one Adriaen van't Hoff, who lived in the latter half of the seventeenth century at Groote Lind, near Rotterdam. His father was a practising physician in that city, his mother the daughter of a wine dealer of Middelharnis. The well-known landscape of Middelharnis, by Hobbema, in the National Gallery, shows the garden where van't Hoff often played in his boyhood.

Van't Hoff was sent to a private school, in which the education seems to have been of a liberal character, the usual scholastic subjects being relieved by sports, games, and physical exercises. Henry, as he was then called, to distinguish him from a brother likewise named Jacob, excelled in mathematics, and received commendation for his work in natural science. His mind, however, was not wholly occupied with his regular school studies, for at this time he was awarded prizes by a local musical society for singing and for pianoforte playing. Long country walks were a favourite recreation, and his letters show both his acute observation of nature and his keen appreciation of scenery. At the age of fifteen he entered the newly founded "Hoogere Burgerschool," a non-classical institution of the type of a German Real-school. Whilst constantly

\* My information has been mostly derived from "J. H. van't Hoff's Amsterdamer Periode 1877—1895," by W. P. Jorissen and L. Th. Reicher (Heider, 1912), and in particular from the interesting biography by Professor Ernst Cohen, "Jacobus Henricus van't Hoff, sein Leben und Wirken" (Leipzig, 1912). Both of these works contain full bibliographies.



near the head of his class, he never succeeded in reaching the first place, if, indeed, he ever tried.

Here he received his first instruction in chemistry. A school companion relates that they were taught according to the old system of formulæ, the formula of water, for example, being HO, although they were told in the highest class that a new formulation with  $H_2O$  was beginning to make headway. Practical instruction in chemistry was given in the school, and this evidently interested young van't Hoff, for he with some companions secretly repaired to the school on Sundays to finish their class exercises, and to perform additional unauthorised experiments. As they, boylike, enthusiastically chose to work with highly poisonous or explosive substances, their private investigations, when discovered, were brought to an abrupt end. Van't Hoff, however, continued his experiments at home, and conducted them on business-like lines, as he is reported to have charged spectators a small fee, which was expended in the purchase of fresh apparatus and material. A few months before van't Hoff completed his curriculum, the chemist Hoogewerff was appointed head of the school, and gave a sketch of the development of theories of organic chemistry, which, although too far advanced for the majority of the scholars, was welcomed and appreciated by van't Hoff. His leaving certificate reads as follows:

Mathematics and mechanics .....	Excellent
Physical science.....	Very good
History, etc. ....	Good
Languages and literature.....	Satisfactory
Drawing .....	Satisfactory.

The following two years were spent by van't Hoff at the Polytechnic School of Delft. He had not yet decided what line of life he would take up, beyond that it should be practical. A holiday experience in a sugar factory, however, convinced him that technical chemistry was a somewhat monotonous occupation, and his inclination turned more and more towards pure science. He therefore on returning to the Polytechnic studied with increased zeal, and to such purpose that he received his diploma at the end of the second year, whereupon he left Delft for the University of Leiden.

What chiefly weighed with van't Hoff in moving to Leiden was the better opportunity afforded there for the study of the higher mathematics, the want of which he had greatly felt at Delft. At the University he frequented student society but little. On his rare appearances at the Debating Club, however, his comments on questions of the day and on topics of art or science provoked and enlivened discussion. Freedom and originality of thought were

even then characteristic of him. Indeed, he complained in later years of his University studies that they were too matter-of-fact, took too little account of his being a man and not a mere organ for the acquisition of knowledge; and declared that under their influence he would have become a dried and shrivelled scientific conglomerate had it not been for the counter influence of the intensely subjective and personal Byron. The writers who influenced him at this impressionable period of his life were, on the philosophic-scientific side, Comte and Whewell, on the literary side, Burns and Heine. But Byron was his favourite and hero. References to Byron, quotations from Byron, abound in his letters, and together with much verse in his native tongue van't Hoff wrote many Byronic stanzas in English.

Van't Hoff now definitely decided on the study and prosecution of chemistry as his work in life, and since Leiden offered no special facilities in the subject, he passed his candidate's examination, a necessary step towards the doctorate, and left the University at the end of a year.

Kekulé's fame attracted him to Bonn. The romantic surroundings of the Rhine University town made a strong appeal to him. He wrote later: "In Leiden all was prose—the town, the country, the people. In Bonn all is poetry."

Only a year was spent by van't Hoff in Bonn. That he became unsettled, melancholy, even bitter, is clearly shown by the tone of his letters. He found Kekulé unsympathetic, but made a lasting friend in Walthère Spring, of Liège.

There can be little doubt that Kekulé's teachings on the constitution of organic substances deeply interested van't Hoff, and it was on Kekulé's advice that he continued his scientific studies elsewhere instead of accepting a technological or teaching post. van't Hoff's choice fell on the "Ecole de médecine," in Paris, where the genial Adolphe Wurtz directed the studies of his enthusiastic pupils, but before proceeding to France he entered the University of Utrecht for three months in order to pass the doctoral examination preliminary to the doctorate. The most noteworthy circumstance of van't Hoff's sojourn in Paris is that there he made the acquaintance of the Alsatian, Joseph Achille Le Bel, who a year later was to share with him the credit of the invention of the asymmetric carbon atom. van't Hoff apparently did little in the way of practical research while in Paris, and it is recorded of him, "Il était si tranquille qu'on ne faisait pas grande attention à lui."

In order to obtain his doctor's degree, van't Hoff re-matriculated in the University of Utrecht in October, 1874, and was promoted to his doctorate in December of the same year. His dissertation

was entitled "A Contribution to our Knowledge of Cyanacetic Acid and Malonic Acid." It was of a routine character, and contained nothing beyond the powers of an ordinary advanced laboratory student. This is at first sight surprising, for van't Hoff had in the preceding September issued as a pamphlet his famous paper on space-formulæ. The original pamphlet was in Dutch, and bore the title, "An attempt to extend to space the present structural chemical formulæ, with an observation on the relation between optical activity and the chemical constitution of organic compounds." It argues well for the sound common sense of the young van't Hoff that he presented a humdrum piece of practical work for his dissertation rather than the startling innovation contained in his pamphlet, for the latter might have had an even worse fate than the equally famous thesis of Arrhenius, containing the first statement of the theory of electrolytic dissociation.

In giving this sketch of van't Hoff's educational career, I have made no attempt to treat it otherwise than in a superficial, mainly topographical, manner; and this because I fancy that the accidents of his education had little influence on his mental development. Now at the beginning of his productive career we find him a quiet, unassuming young man of twenty-two, with a physique by no means robust; reserved, but of agreeable manners; cultivated on many sides; with a taste for the writing of verse and for natural science, in particular entomology. He differed from the bulk of his academic contemporaries in being essentially a man of ideas, a thinker. He had pondered over the properties of the atoms, on their actions on one another at small distances, and over the problem of how the chemical and physical properties of compound molecules were to be conceived as a function of the nature of the constituent atoms and of their arrangement. The first tangible result of this cogitation was the laying of the foundation of stereochemistry.

It is a constant phenomenon, and always a fresh surprise in the history of science, to find a pioneer, capable, one might think, of any mental step, stopping short by a hand's breadth of some important discovery or generalisation. The driving force of the original idea exhausts itself, or the general state of knowledge fails in some particular, and years may have to elapse before a fresh mind with a new stimulus, and possibly a different goal, can take the required step. The early history of stereochemistry illustrates this peculiarity of scientific advance in striking fashion.

In a lecture published in 1860 Pasteur said: "We know, on the one hand, that the molecular structures of the two tartaric acids are asymmetric, and, on the other, that they are rigorously the

same, with the sole difference of showing asymmetry in opposite senses. Are the atoms of the right acid grouped on the spirals of a dextrogyrate helix, or placed at the summits of an irregular tetrahedron? We cannot answer these questions." The ideas of the quadrivalent carbon atom and of molecular structure based upon it were still too novel and also too remote from Pasteur's practical line of thought, to enable him to take the short but, as it turned out, difficult step to the asymmetric carbon atom.

That the necessity for space-formulae became increasingly felt is evident from the following quotations.

In 1867 Kekulé wrote: "The incompleteness of the old models may be avoided if, instead of arranging the four affinities of the carbon atom in a plane, we place them in the directions of hexagonal axes, so that they run out from the spherical atom and end in the planes of a tetrahedron."

A definite example of the use of space-formulae is given by Paternò in 1869, who writes as follows:

"Three isomerides,  $C_2H_4Br_2$ , supposing that they really exist, can be easily explained, without the necessity of assuming with Butlerow a difference amongst the four affinities of the carbon atom, if we postulate that the four valencies of the atom of carbon are arranged in the sense of the four angles of a regular tetrahedron: then the first modification would have the two atoms of bromine (or any other univalent group) attached to the same atom of carbon; whilst in the other two modifications, the two atoms of bromine would be each attached to a different carbon atom, with the difference that in one case the two atoms of bromine would be symmetrically arranged, and in the other not."

Wislicenus in the same year clearly indicates the general nature and mode of solution of the problem in connexion with the lactic acids: "Facts like these will force us to explain the difference between isomeric molecules with the same structural formula by means of a different arrangement of their atoms in space, and to seek for definite ideas concerning this," a statement which he reiterates and emphasises in 1873.

These definite ideas were given practically at the same time by van't Hoff and by Le Bel, the former publishing his pamphlet in September, 1874, and the latter a paper in the *Bulletin de la Société Chimique* in November of the same year. One would naturally imagine that the idea which gave the key to the problem must have originated in one of the frequent discussions in Wurtz's laboratory, for here we have two young men parting at the end of June, and a few months later publishing separately a notion which was at the time generally regarded as something entirely novel and

revolutionary. Yet van't Hoff tells us that no communication on the subject had passed between them. He says: "That shortly before this we had been working together in Wurtz's laboratory was purely fortuitous; we never exchanged a word about the tetrahedron there, though perhaps both of us cherished the idea in secret. To me it had occurred the year before, in Utrecht, after reading Wislicenus's paper on lactic acid."

In view of the passages I have quoted above from earlier workers, it might almost be asked: What, then, did van't Hoff and Le Bel discover? Wherein lies the merit of their work that they should be acclaimed as the originators of stereochemistry when the problem and the fundamental ideas seem to have been so clearly enunciated before them? On the one hand, the idea of the asymmetric structure of optically active molecules was given by Pasteur; on the other, Paternò uses tetrahedral carbon atoms to explain a case of isomerism in much the same way as they would be used to-day, except that he regards the carbon tetrahedra as not being capable of rotation round the axis joining their centres. Separate, these ideas remained unproductive; correlated, they became endowed with marvellous fertility. Van't Hoff and Le Bel's great contribution to stereochemistry was to define the conditions under which the asymmetric structure appeared, namely, when the carbon atom was attached to four different groups. Van't Hoff, in addition, boldly adopted the tetrahedron as the formal representation of the carbon atom in this new aspect; Le Bel, whose considerations are more general, only mentions it once in his paper. Not only did they state the bare principle, however; they showed it was a living one, drew deductions from it, applied it on all sides, and delivered it, in short, as an effective instrument into the hands of their fellow-workers in chemistry. Otherwise, like Avogadro's principle, it might have been forgotten, and for years perhaps have awaited some Cannizzaro to rediscover or revivify it.

It is of interest to quote van't Hoff's own words as to the origins of his conception and that of Le Bel, and as to the points in which they differed:

"On the whole, Le Bel's paper and mine are in accord; still, the conceptions are not quite the same. Historically, the difference lies in this, that Le Bel's starting point was the researches of Pasteur, mine those of Kekulé.

"The researches of Pasteur had made plain the connexion between optical activity and crystal-form, and had led to the idea that the isomerides of opposite rotatory power correspond with an asymmetric grouping and to its mirrored image. Indeed, the possibility of a tetrahedral grouping was suggested. Le Bel closely follows Pasteur,

then, when he sees this grouping in the four atoms or radicles - inactive bodies all different—united to carbon.

My conception is, as Baeyer pointed out at the Kekulé festival, a continuation of Kekulé's law of the quadrivalence of carbon, with the added hypothesis that the four valencies are directed towards the corners of a tetrahedron, at the centre of which is the carbon atom.

"Practically our ideas, so far as they concern the asymmetric carbon, amount to the same thing—explanation of the two isomerides by means of the tetrahedron and its image, disappearance of this isomerism when two groups become identical, through the resulting symmetry and identity of the two tetrahedra."

Le Bel's general treatment was more purely geometrical and in certain ways more thorough than that of van't Hoff, which was better calculated to appeal to chemists, and, indeed, gave the stamp to stereochemistry in its subsequent development. In detail the following points of difference between the authors may be noted. Le Bel accounts for the existence of internally compensated inactive forms, such as mesotartaric acid; van't Hoff, by means of the tetrahedra, clearly explains the nature of unsaturated inactive isomerides, such as maleic and fumaric acids.

The following lines contain a brief résumé of the original pamphlet of September, 1874. Van't Hoff shows that if we imagine the four affinities of the carbon atom to lie in a plane, the groups attached to them being fixed, and their positions not interchangeable, a great many more isomerides are predicted than actually exist. If, on the other hand, the affinities are not in a plane, but directed to the summits of a tetrahedron from its centre, the number of compounds predicted in general coincides with the number of compounds existing. His chief statements are given in the following terms:

(a) If the four affinities of a carbon atom are satisfied by four different univalent groups, two and not more than two tetrahedra are obtained, of which one is the mirror image of the other and cannot be superposed on it; that is, we encounter two isomeric structural formulae in space.

(b) Each carbon compound which in the dissolved state effects a rotation of the plane of vibration of a polarised ray, contains an *asymmetric* carbon atom, that is, one whose affinities are satisfied by four different univalent groups. As examples, he gives lactic acid, aspartic acid, asparagine, and malic acid, with one asymmetric carbon atom; tartaric acid with two; the sugars, mannitol, etc., with at least one. Further, camphor and borneol, according to Kekulé's formulation, contain an *symmetric* carbon atom, and are correspondingly active.

The derivatives of optically active compounds lose their activity if the asymmetry of all the carbon atoms disappears; for example, inactive maleic acid from active malic acid, inactive succinic acid from active tartaric acid, inactive cymene from active camphor.

In a list of compounds the formulæ for which contain an asymmetric carbon atom, there are many cases in which the compound is not active. This may be accounted for in one of the following ways:

1. The compound may be an inactive mixture of two equally and oppositely active isomerides.
2. If the activity is small, it may be lost in the experimental error.
3. The condition "asymmetric carbon atom" may not in itself be sufficient, the nature of the different groups being of moment as well as their mere difference.

The principle that an optically active compound probably contains an asymmetric carbon atom gives the means of choosing between possible formulæ; for example, optically active primary amyl alcohol must have the formula  $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{C}(\text{H})\cdot\text{CH}_2\cdot\text{OH}$ . There is a certain degree of probability that an inactive compound contains no asymmetric carbon atom. Thus, the formula of citric acid is probably  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and not  $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

Formulæ are given for the simplest optically active monohydric alcohol, monobasic acid, dihydric alcohol, saturated hydrocarbon, and aromatic hydrocarbon; and attention is drawn to the fact that there are no optically active normal hydrocarbons, alcohols, or acids.

(c) If two doubly bound carbon atoms are each united to two radicles which differ from each other, two isomerides, hitherto unforeseen, are predicted; for example, maleic and fumaric acids.

In van't Hoff's pamphlet the carbon tetrahedra are figured exactly as they are met with now in text-books of organic chemistry.

A French translation of the paper appeared soon afterwards in the *Archives Néerlandaises*, and a condensed French account in the *Bulletin de la Société chimique*. Finally, a much expanded French pamphlet, "*La chimie dans l'espace*," was published at Rotterdam in May, 1875.

Disappointment followed the publication. Instead of his hypothesis provoking discussion, as he had hoped, it was received by the majority of chemists with indifference, if not with coldness. Wurtz, Spring, and Louis Henry wrote warm acknowledgments of its receipt, but made no attempt to discuss or criticise. Berthelot, whilst admitting the general interest of van't Hoff's formulæ, took

up the ground that a complete representation of constitution involved a representation of the rotatory and vibratory movements of the atoms and groups, and was disposed to attribute optical activity to these movements. The physicist, Buys Ballot was the first to give serious attention to van't Hoff's theory, and in the *Maandblad voor Natuurwetenschappen* he published an open letter to van't Hoff, who replied in a paper (November, 1875), discussing many interesting points which had been raised in the letter. He gives, for example, the configurations of the ten isomeric saccharic acids. A cordial letter from Wislicenus then followed, suggesting that the pamphlet should be translated into German, which was done by Herrmann, and issued in 1877 under the title *Die Lagerung der Atome im Raume*, with a preface by Wislicenus. The German version, which differs in many ways from the original, was widely read, and van't Hoff's ideas now began to gain ground. Strenuous opposition by Kolbe, who at that time was tilting at graphic formulae of every sort in a series of lively articles in the *Journal für praktische Chemie*, perhaps, if anything, increased their vogue by drawing more attention to the subject.

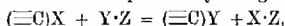
Meanwhile van't Hoff had graduated, and was on the look-out for a situation. He failed to obtain any teaching post as science master in a school, but in March, 1876, he succeeded in becoming assistant in the Veterinary College of Utrecht, there to teach chemistry and physics. He had command of good apparatus, and during the two years of his tenure of the office he worked at a variety of subjects, the substances obtained from storax claiming much of his attention. He wrote several stereochemical papers, one on carbon rings, one on Ladenburg's benzene formula, one on the direction of the valencies of the nitrogen atom, and one on the connexion between optical activity and constitution.

To this period belongs his book, "*Ansichten über die organische Chemie*," the preface of which is dated Utrecht, October, 1877. In itself the book is almost unreadable, but it affords the clearest evidence of the author's independence of thought, his keen eye for essentials, and the painstaking way in which he sought to isolate materials and problems of pure chemistry from the traditional associations which obscured them. The first part is purely systematic, and treats of the physical and chemical properties of organic substances regarded and classified as derivatives of methane. In the introduction to the second part (published in 1881), he expresses himself as follows:

"The purpose of the second part is to obtain a knowledge of the chemical nature of carbon in itself and of the changes which it undergoes when the element combines with other atoms or



groups of atoms. To succeed in this purpose we must obtain a general view of the chemical reactions in which the carbon atom plays a part, and the changes in physical character which accompany them. If such a reaction is expressed by the general equation:



the knowledge of the reaction must include a knowledge of the heat change which accompanies the reaction, and of the velocity with which it takes place under given conditions, whilst a knowledge of the changes of property is attained by comparison of the physical nature of  $(\equiv C)X$  and  $(\equiv C)Y$ . The reaction expressed above in general form may be followed out for particular carbon compounds  $(\overset{\alpha}{\underset{\beta}{\overset{\gamma}{\text{C}}}})X$  in the same two directions. What ultimately appears as independent of  $\alpha, \beta, \gamma$  is the expression of the chemical nature of carbon in itself; the difference due to the changes of  $\alpha, \beta, \gamma$  are, on the other hand, regarded as the changes which carbon undergoes when it combines with other atoms or groups of atoms."

In the text of the second part we find the beginnings of those studies in chemical thermodynamics and affinity which were afterwards pursued to such good purpose.

In September, 1877, van't Hoff was appointed lecturer in chemistry in the Town College of Amsterdam, which a month later was raised to the dignity of a State University. In June, 1878, at the age of twenty-six, he became ordinary Professor of Chemistry, Mineralogy, and Geology; and six months later he married Johanna Francina Mees, the daughter of a Rotterdam merchant, whom he had known from early youth.

Van't Hoff spent eighteen years in the University of Amsterdam. Although the old laboratory in which he worked was small and inconvenient, he refused a call in 1887 to the newly created Chair of Physical Chemistry in Leipzig, eventually filled by Ostwald. His teaching duties were onerous. With two assistants he had to give instruction in organic and inorganic chemistry, crystallography (which he had studied with Groth), mineralogy, geology, and palæontology, and to conduct practical classes for 100 medical and 20 science students. Notwithstanding this, the amount of practical work he executed and supervised was very great. The atmosphere of his laboratory may be described in the words of his assistant, van Deventer. "Whoever knows the Amsterdam laboratory knows that things do not take place there in any ordinary way. There is something mystical, something uncanny in the air. And this demonic something is the belief—one might call it the superstition if success had not so often followed it—the belief of van't Hoff that his fundamental idea, the analogy between chemical

and physical phenomena, is profoundly true." Elsewhere van Deventer says: "It must be said that van't Hoff's work is in many ways more French than German. Soundness and solidity he certainly values, but he is in love with the idea in its general form, and his proofs are directed more towards establishing his idea in the world as a great rough block that cannot be overthrown, than to modelling and rounding it off—that he willingly leaves to others.

"This love of the idea is often found, too, in the experimental method which he adopted. Transition points were studied with an instrument which a well-trained physicist would only have used for preliminary experiments. Van't Hoff used it for the decisive investigation, and the proof is unimpeachable."

It is characteristic of van't Hoff's devotion to the idea that he chose as the subject of his inaugural address in Amsterdam, "The rôle of Imagination in Science," and strove to show how great a part imagination played in scientific investigation. He drew attention to the imposing number of scientific men with a leaning towards poetic and romantic invention, and closed his address with a quotation from Buckle: "There is a spiritual, a poetic, and, for aught we know, a spontaneous and uncaused element in the human mind, which ever and anon, suddenly and without warning, gives us a glimpse and a forecast of the future, and urges us to seize truth as it were by anticipation."

Following out the line of thought already indicated in his introduction to the "*Ansichten*," van't Hoff investigated various types of reaction velocity and chemical equilibrium, which he collected in his *Etudes de dynamique chimique*, published in 1884. It is true that much had been done by others in these fields of investigation; for example, in velocity by Harcourt and Esson and by Goldberg and Waage, and on the thermodynamical side by Horstmann and by Willard Gibbs, although the work of the latter was then unknown to van't Hoff, as indeed it was to chemists generally. Van't Hoff, however, systematised, exemplified, and applied the principles involved, and, in fact, left the subject of chemical dynamics much in the state in which we find it to-day. For example, he classified reactions into unimolecular, bimolecular, termolecular, according to the number of molecules taking part in the transformation. He showed how to determine the number of molecules taking part in a chemical action, and investigated secondary actions and disturbing influences. He discussed "temperature of inflammation." He introduced the symbol  $\rightleftharpoons$  for reversible actions. He introduced and illustrated the term "transition point," and showed the close analogy between the chemical "transition point" and the physical melting point, in

particular as regards the effect of pressure. He stated clearly the *principe de l'équilibre mobile* as follows: "Every equilibrium between two systems is displaced by fall of temperature in the direction of that system in the production of which heat is developed." He showed that Berthelot's *principe du travail maximum* is only strictly true at the absolute zero. Finally, he devoted the last section of the book to a study of chemical affinity. He shows how affinity may be measured by electromotive force, how at a point of transition the work of affinity is zero, and constantly uses the important equation:

$$\frac{d \log_e K}{dT} = \frac{q}{2T^2}$$

although he does not prove it, merely stating that it had been deduced in a rigorous manner from the principles of thermodynamics. I remember having read these *Études* in 1885 or 1886, and I can well recall the mingled feeling of revelation and bewilderment which the book produced on me. I had perused such books on theoretical and physical chemistry as were then available, but had derived comparatively little satisfaction from them. Here, I thought, was the real thing at last, hard to comprehend, certainly, but something definite. What I understood was excellent. What I did not quite succeed in understanding seemed, somehow, even better.

Arrhenius, at that time personally unknown to van't Hoff, in reviewing the *Études*, wrote as follows: "This work, which is of the greatest interest, consists of two essentially different parts: the first experimental, the second theoretical. The former is, however, of quite subordinate significance, notwithstanding the many peculiar and interesting phenomena discussed in it. In the latter portion the author displays an extraordinary talent for bringing a great series of different facts under one point of view, and he succeeds with relatively scanty experimental material in developing an imposing and harmonious scheme for the whole subject of chemical influence and action. Although the author has already gained a great name by his power of wresting secrets from Nature, his former efforts are placed entirely in the shade by this work. An enormous perspective has been opened up for future investigation. There are, however, but few workers in the promising field, though possibly this will shortly be remedied; for since Helmholtz, who sets the fashion in physical circles, has turned his attention of late years to such subjects, it will probably not be long before eager investigators are working at them."

A few years later this prediction was fulfilled, chiefly through the

instrumentality of Ostwald, the first occupant of the chair of physical chemistry in Leipzig.

In the *Études* we have the first appearance of osmotic pressure from the physico-chemical point of view. Through his distinguished countryman, the botanist, Hugo de Vries, van't Hoff had become acquainted with Pfeffer's osmotic measurements. He at once saw the thermodynamic importance of the conception, and used it in conjunction with the lowering of vapour pressure to calculate the affinity of certain salts for their water of crystallisation. In the following year (1885) he published in the *Archives néerlandaises* a paper bearing the title "*L'équilibre chimique dans les systèmes gazeux ou dissous à l'état dilué, gazeux ou dissous*"; and in 1886 he published in the Transactions of the Swedish Academy three memoirs, entitled "*Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous*," "*Une propriété générale de l'équilibre chimique*," and "*Conditions électriques de l'équilibre chimique*."

In these papers van't Hoff had arrived at the complete analogy between gases and substances in dilute solution. He tells us that in giving the proof of his equation:

$$\frac{d \log K}{dT} = \frac{q}{2T^2},$$

by means of reversible cycles for dilute gaseous systems, it occurred to him that with the help of semi-permeable membranes all the reversible processes which make the application of thermodynamics to gases so simple might as readily be applied to substances in dilute solution. It at once followed that the osmotic pressure must vary with the temperature according to Gay-Lussac's law. Pfeffer's measurements for 1 per cent. sugar solutions seemed to confirm this conclusion, although they were scarcely sufficiently accurate to afford absolute proof of the relation. Then Pfeffer had shown that the osmotic pressure was proportional to the concentration, that is, Boyle's law was followed as well as Gay-Lussac's, and it was possible to write for dilute solutions an equation similar to that for gases, namely:

$$PV = RT.$$

The only thing left was to calculate  $R$ , the solution-constant, and compare it with the gas-constant. van't Hoff did this for sugar solutions from Pfeffer's measurements, and found to his surprise that the value was identical with that of the gas-constant. At first he looked upon this identity as a mere coincidence, but further consideration showed it to be fundamental, and that osmotic and gaseous pressure were always equal, when molecular concentration and temperature were equal, that, in short, Avogadro's law held without alteration for substances in dilute solution as well as for

gases, and that the molecular weights of dissolved substances could be determined on the same theoretical grounds as those of gases.

Raoult had in the meantime shown empirically how molecular weights might be determined from the lowering of the freezing point, and van't Hoff was now in a position to give the theoretical justification of this method, by deducing thermodynamically from Avogadro's law and the properties of the solvents, the quantitative rules for the lowering of vapour tension, the depression of the freezing point, and the elevation of the boiling point of solutions.

It should be noted that van't Hoff was from the first very careful to point out that all these relations were strictly applicable only to very dilute solutions, to "ideal solutions," as he calls them, and that he never claimed the theory of osmotic pressure as a complete theory of solutions. He definitely stated, indeed, in his address to the German Chemical Society (*Ber.*, 1894, 27, 15): "It is not even necessary to choose osmotic pressure as the starting point [of these relations]; the whole might be deduced as readily from Henry's law or from Raoult's law. Only osmotic pressure is a very simple and handy expression for the whole behaviour, and its physical meaning is very readily stated and grasped, thus: If a substance in a state of dilution exists in surroundings into which it can expand by diffusion, then, at a given temperature, the pressure which will prevent this diffusion is dependent only on the number of dissolved molecules, and not on the nature of the medium." To van't Hoff's mind the real theory of the intimate nature of solutions begins where the simple laws *cease* to be obeyed. In a sense this is true, and a good example of what it means is afforded by the early history of the osmotic pressure theory. Van't Hoff had found that the value of the osmotic constant was not for all substances equal to the gas constant  $R$ . With his customary skill in handling such matters, he wrote the equation for these substances as follows:

$$PV = iRT,$$

using a factor  $i$ , which was thus the measure of the abnormality of the substance. The work of Arrhenius supplied two years later the explanation of the abnormality in the case of the great class of electrolytic solutions. The abnormally great value of  $i$  for such solutions was held by Arrhenius to be due to the molecular concentration in such solutions being greater than had theretofore been accepted. According to his theory of electrolytic dissociation, some of the original dissolved molecules had split up under the influence of the solvent into simpler positive and negative ions, so that the total number of molecules was increased, the excess of  $i$  over 1 being the measure of the increase. This, then, is a contribution

to the theory of solution for a certain class of solutions, and it appears to me that every future contribution will be of the same nature, dependent on the nature of the solvent and dissolved substance, and therefore of a different scope entirely from van't Hoff's generalisation.

Two distinct points may be noted in connexion with the papers just referred to. First, there is the introduction of the conception of osmotic pressure into thermodynamics generally, and the use of semipermeable membranes for reversibly changing the concentration of solutions. Second, there is the special application of the conception in deducing the simple general laws for ideal solutions. As van't Hoff himself has said, it would be possible to substitute for osmotic pressure in the purely thermodynamical treatment some other magnitude which is proportional to it, but it may be confidently predicted that the conception once introduced, and through which such advances have been made, will never be discarded.

One often encounters among chemists the impression that van't Hoff was essentially a mathematician, or at least a man of mathematical formulae, who cared nothing for atoms or molecules. Nothing could be further from the truth. Van't Hoff's actual knowledge of mathematics is surpassed, I fancy, by the average honours B.Sc. student of to-day. His ability in this direction lay rather in the power of handling the mathematical tool for his own purposes. But, as is apparent from the passages I have already quoted, the essential thing for him is the reciprocal action and influence of atoms and molecules. The nature of osmotic pressure, as well as its law, was of profound interest to him. He first of all conceived it as having its origin in the mutual attractions of solvent and solute molecules, but soon discarded this view for one of molecular bombardment in analogy with the kinetic theory of gases. This kinetic theory of the origin of osmotic pressure, despite criticisms, still seems superior to any other that has been proposed, and awaits further development.

Although, as has been said, the papers comparing dilute substances with gases were published in 1885, it was only in 1887 that the ideas became generally known. Ostwald, the organiser of the campaign in favour of the new ideas of van't Hoff and Arrhenius, associated himself with the former in founding the *Zeitschrift für physikalische Chemie*, in the first volume of which the fundamental papers of the two pioneers of modern physical chemistry appear.

With the foundation of this journal van't Hoff's scientific life may be said to have reached its climax. His fame became world-wide, and many honours awaited him. A new chemical laboratory, built according to his design, was opened in 1891, and many

foreign students visited him who could not have been accommodated in the old building. With the increase of his department, van't Hoff found that he had to devote more and more time to administrative duties, as is the universal experience of the heads of large laboratories. He naturally disliked to see his leisure for personal research slip away from him, and asks, "Besides men whose duty it is to teach, and who, if they have time and inclination for it, may prosecute research, is there not room for another class of men whose duty should be to investigate, and who, if they pleased, might also teach?" In the spring of 1895 a position of the latter kind was offered to him in Berlin. Great efforts were made by his colleagues in the University of Amsterdam to induce the Government of the Netherlands to retain him in Holland on similar terms, but these efforts were unsuccessful. Van't Hoff, in the spring of 1896, moved to Berlin, as a member of the Prussian Academy of Sciences and as a Professor in the University. His academic duties were of the lightest, one lecture a week being all that was required of him. His research work was carried out in a small laboratory situated in a pleasant suburb of Berlin. Here his chief collaborator was his friend and former pupil, Meyerhoffer. Often in conjunction with younger men, they studied the physical chemistry of the Stassfurt salt deposits, and similar phase-rule problems.

Such work, though of much general and special interest, is not to be placed on a par with van't Hoff's former achievements. It is true that in plan and in performance it may be taken as a model for an investigation on the grand scale, yet one cannot but entertain the feeling that a lesser man than van't Hoff, for example, his own countryman, Bakhuis Roozeboom, might have carried it to an equally successful conclusion. The conception of solid solutions (1890) is van't Hoff's last contribution to novel chemical ideas.

Van't Hoff had now more leisure, not only for practical research, but for travel. He has left an interesting journal of his impressions of America in 1901. In December of the same year he journeyed to Stockholm to receive the first Nobel Prize for Chemistry; and it may be recalled that he delivered the Raoult Memorial Lecture here in 1902.

The death of Meyerhoffer in 1906 affected him deeply, and later in the same year his own health began to give way. He himself writes: "My health, almost invariably good, seemed in the summer of 1906 to be even better than usual. In early spring I had visited the neighbourhood of Vesuvius at the time of the eruption, and returned home rejuvenated. Hay-fever, for many years my bugbear, had vanished, and it appeared as if my Bonn student days, with all their poetry, had, comet-like, returned. And yet I found in

all this something abnormal, and recalled to mind a saying of a former medical colleague, that a feeling of specially good health in one's later years is a bad omen. In October came the first indications of what six months later developed into an illness which for a time laid me aside from all work." From that date van't Hoff had to spare himself, a thing peculiarly distasteful to a man of his active mind and temperament. He brought his work on the salt-deposits to a close, and devoted himself to the lighter labour of revising some of his older books, and projecting new ones.

His last scheme of investigation was a study of the intimate nature of the chemical processes occurring in plants. To this end he began in 1909 a research on reversible enzymatic action, and published a preliminary account in the *Sitzungsberichte* of the Prussian Academy (October, 1909, and November, 1910). These admirable fragments show a last flash of van't Hoff's illuminating genius. The clearness of the theoretical conceptions, the simplicity of the experimental execution recall the best period of his activity. He proved that the action of the enzyme emulsin in the formation and decomposition of glucosides was that of an ordinary catalyst in accordance with the mass-action law, the rates of the reverse reactions alone being affected and the point of equilibrium remaining unchanged.

The last experiments were carried out in a small private laboratory which had been built for him on the Imperial Crown-lands at Dahlem. Here from time to time he was able to do a little work, but the progress of his malady slowly enfeebled him. The entry in his diary for December 11th, 1910, reads, "Article on 'Teaching and Research' finished: a last effort." On the evening of March 1st, 1911, he died peacefully.

With no great mathematical or experimental attainment, with no striking gift as a teacher, van't Hoff yet influenced and moulded the current thought, and even much of the practice, of chemistry for decades. He set out with a clear scientific ideal. Native inspiration and unflagging ardour in pursuit of this ideal led him to the discovery of principles of the widest and most far-reaching import. He was, in my judgment, the greatest chemical thinker of his generation. If any should dispute this judgment, I can only reply that our science is indeed favoured when such dispute is possible.

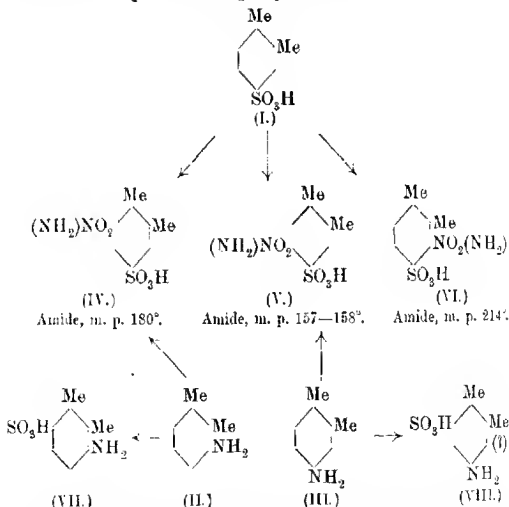


CXX.—*Derivatives of o-Xylene.*

By JOHN LIONEL SIMONSEN.

In spite of the careful investigation of Crossley and Renouf (T., 1909, 95, 202), the preparation of 3-nitro-*o*-xylene is still a somewhat laborious process. As the author required a considerable quantity of this substance for certain experiments, it occurred to him that it might possibly be obtained more readily by the nitration of *o*-xylene-4-sulphonic acid and subsequent elimination of the sulphonic acid group. Although this expectation was not realised, the experiments seem of sufficient importance to warrant publication.

When *o*-xylene-4-sulphonic acid is treated with nitric acid under the conditions described in the experimental part of this paper (p. 1151), the three isomeric nitro-*o*-xylene-4-sulphonic acids are formed. The orientation of these acids is a matter of considerable difficulty, owing to the fact that no method could be devised to eliminate the sulphonic acid group:



On reduction, the nitro-sulphonic acids are converted into the corresponding amino-acids, and it was found possible to orientate these acids in the following manner. When *o*-3-xylydine (**(II.)**) is

sulphonated, it yields a mixture of two sulphonic acids, which may be separated by means of their barium salts. Since one of these acids was completely different from the amino-acids (IV, V, or VI) obtained by the reduction of the nitro-acids derived from *o*-xylene-4-sulphonic acid, it follows that it must be *o*-3-xylylidine-6-sulphonic acid (VII).

The second acid isolated in this sulphonation was found to be identical with the amino-acid obtained by the reduction of the nitro-sulphonic acid, yielding an amide melting at 180°; this acid must therefore possess the constitution indicated by the formulæ IV or VI. In order to decide which of these two formulæ was correct, the amino-acid was diazotised and converted into the xylenolsulphonic acid, which on fusion with potassium hydroxide yielded a dihydroxyxylene giving a purple colour with ferric chloride and a fluorescein when treated with phthalic anhydride. Unfortunately this phenol was not obtained in sufficient quantity to purify, but it probably consisted of 3:5-dihydroxy-*o*-xylene (*Annalen*, 1904, 329, 305). From this it follows that the amino-sulphonic acid must be *o*-3-xylylidine-5-sulphonic acid, and the nitro-acid which yields an amide melting at 180° must be 3-nitro-*o*-xylene-5-sulphonic acid (IV).

In order to determine the constitution of the two remaining nitro-acids the sulphonation of *o*-4-xylylidine was investigated, when it was found that two sulphonic acids were formed. One of these was identical with the amino-acid obtained by the reduction of the nitro-acid, yielding an amide melting at 157–158°. Only one formula is possible for this acid, which must be *o*-4-xylylidine-5-sulphonic acid (V). This was confirmed by eliminating the amino-group from a specimen of the amino-sulphonic acid prepared from *o*-4-xylylidine, when *o*-xylene-4-sulphonic acid was obtained and identified by means of its amide.

As to the constitution of the second acid formed in the sulphonation of *o*-4-xylylidine, it has unfortunately proved impossible to arrive at any definite conclusion. The acid was diazotised and the xylenolsulphonic acid fused with potassium hydroxide, when a dihydroxyxylene was isolated, giving an intense purple coloration with ferric chloride; it was not sufficient for any further investigation. It is probable that this acid is *o*-4-xylylidine-6-sulphonic acid (VIII). An acid possessing this constitution has already been described by Cazeneuve and Moreau (*Bull. Soc. chim.*, 1898, [iii], 19, 21). It was prepared by the sulphonation of *s*-dixylylcarbimide [ $\text{NH}:\text{Me}_2=1:3:4$ ]. This experiment has been repeated, and it has been found that the products are identical with those obtained by the sulphonation of *o*-4-xylylidine. Since, however, *o*-4-xylylidine-

6-sulphonic acid is formed in much the larger amount, it is probable that it was this acid which was described by Cazeneuve and Moreau.

It now only remains to consider the constitution of the third acid obtained by the nitration of *o*-xylene-4-sulphonic acid. There is only one possible formula for this acid, and it must be 3-nitro-*o*-xylene-4-sulphonic acid (VI).

Since the amino-sulphonic acids described in this paper do not possess melting points, and since all attempts to prepare derivatives which might have proved useful for identification purposes proved unsuccessful, it was necessary to identify the acids or their salts by careful examination under a polarising microscope, and I wish to express my thanks to my colleague, Dr. M. Stuart, Professor of Geology, for assisting me in this part of the work.

#### EXPERIMENTAL.

##### 3-Nitro-*o*-xylene-5-sulphonic Acid.

This acid was obtained in the form of its sparingly soluble barium salt by the nitration of *o*-xylene-4-sulphonic acid (see p. 1152). The barium salt was purified by repeated crystallisation from hot water, in which it is only sparingly soluble; it separates on cooling in glistening, prismatic needles, which apparently contain three molecules of water of crystallisation:

0.7974 lost 0.0437 at 110°.  $\text{H}_2\text{O} = 5.5$ .

0.9678 \* gave 0.3409  $\text{BaSO}_4$ .  $\text{Ba} = 20.7$ .

0.4921 † „ 0.1866  $\text{BaSO}_4$ .  $\text{Ba} = 22.3$ .

$\text{C}_{16}\text{H}_{16}\text{O}_{10}\text{N}_2\text{S}_2\text{Ba}_3\text{H}_2\text{O}$  requires  $\text{Ba} = 21.1$ .

$\text{C}_{16}\text{H}_{16}\text{O}_{10}\text{N}_2\text{S}_2\text{Ba}_2\text{H}_2\text{O}$  „  $\text{Ba} = 22.3$ .

Loss of  $2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 5.5$  per cent.

3-Nitro-*o*-xylene-5-sulphonic acid was isolated from the pure barium salt in the usual manner, when it was obtained in slender needles, which were somewhat hygroscopic, the crystals liquefying on exposure to the air. For this reason no attempt was made to analyse the acid. The chloride prepared from the barium salt by treatment with phosphorus pentachloride crystallises from a mixture of benzene and light petroleum in large, glistening, irregular plates, which melt at 69–70°:

0.1247 gave 0.0729  $\text{AgCl}$ .  $\text{Cl} = 14.4$ .

$\text{C}_8\text{H}_8\text{O}_4\text{NSCl}$  requires  $\text{Cl} = 14.2$  per cent.

The amide crystallises from dilute alcohol in fine, hair-like needles, melting at 180°:

0.1059 gave 13.1 c.c.  $\text{N}_2$  at 34° and 760 mm.  $\text{N} = 13.0$ .

$\text{C}_8\text{H}_{10}\text{O}_4\text{N}_2\text{S}$  requires  $\text{N} = 12.2$  per cent.

\* Air-dried.

† Dried at 110°.

*o*-3-Xylidine-5-sulphonic Acid.

(1) From 3-Nitro-*o*-xylene-5-sulphonic Acid.—When the nitro-sulphonic acid is reduced with tin and hydrochloric acid, only a very small yield of the amino-acid is obtained, owing to the simultaneous formation of chloro-derivatives. Reduction by means of an alkaline solution of ferrous sulphate was found, however, to give good results. In one such experiment, the barium salt (3.6 grams) was dissolved in hot water, and treated with an aqueous solution of the calculated amount of ferrous sulphate, barium hydroxide being added until the solution was just alkaline. After heating on the water-bath for two hours, the excess of baryta was removed by carbon dioxide, and the filtered solution concentrated, when the barium salt (2.8 grams) separated in slender needles. For analysis it was purified by crystallisation from a little water:

0.0555 lost 0.004 at 120°.  $H_2O = 4.7$ .

0.2038 \* gave 0.0821  $BaSO_4$ .  $Ba = 23.7$ .

0.0818 † „ 0.0338  $BaSO_4$ .  $Ba = 24.3$ .

$C_{10}H_{20}O_6N_2S_2Ba \cdot 3H_2O$  requires  $Ba = 23.4$ .

$C_{10}H_{20}O_6N_2S_2Ba \cdot 1\frac{1}{2}H_2O$  „  $Ba = 24.3$ .

Loss of  $1\frac{1}{2}H_2O$  requires  $H_2O = 4.6$  per cent.

Barium *o*-3-xylidine-5-sulphonate is excessively soluble in cold water, and shows very little tendency to crystallise. It is also characterised by the fact that it reddens very rapidly on exposure to the air.

*o*-3-Xylidine-5-sulphonic acid crystallises from hot water, in which it is fairly readily soluble, in slender needles radiating from a centre containing apparently one molecule of water of crystallisation, which is not lost at 100°. Like its barium salt, it is characterised by the extreme rapidity with which it reddens on exposure to the air, the change being much more rapid than in the case of its isomerides. It does not melt or decompose at 315°:

0.1363 gave 8.0 c.c.  $N_2$  at 32° and 762 mm.  $N = 6.3$ .

$C_8H_{11}O_3NS \cdot H_2O$  requires  $N = 6.4$  per cent.

(2) From *o*-3-Xylidine.—From the sulphonation products of *o*-3-xylidine (see p. 1152), a barium salt was isolated which possessed all the properties of the barium salt described above, and a careful microscopic examination showed that they were identical. No difference either could be detected in the amino-sulphonic acid isolated from this barium salt. Both the barium salt and the free acid showed the property of rapid reddening on exposure to the air which is so characteristic of this substance.

*Diazotisation of o*-3-Xylidine-5-sulphonic Acid.—In order to pre-

\* Air-dried.

† Dried at 120°.

pare *o*-3-xylenol-5-sulphonic acid, the amino-acid (1.7 grams) was dissolved in water, and after the addition of barium nitrite (0.7 gram), sulphuric acid (0.74 gram) was gradually added to the well-cooled mixture. After remaining in the cold for one hour, the mixture was heated on the water-bath until all evolution of nitrogen had ceased (about thirty minutes). The excess of sulphuric acid was removed by the calculated quantity of barium carbonate, the solution filtered and evaporated, when *o*-3-xylenol-5-sulphonic acid was obtained as a viscid oil, which showed no signs of crystallising. When fused with potassium hydroxide at 320–330°, very little charring took place, and a dihydroxyxylene was isolated in the usual manner, which gave with ferric chloride a purple coloration, and after heating with phthalic anhydride, its alkaline solution was strongly fluorescent. Owing to the very small yield, this compound could not be obtained in a pure state, but there can be no doubt that it was 3:5-dihydroxy-*o*-xylene (*Analeu*, 1904, 329, 305).

#### 3-Nitro-*o*-xylene-4-sulphonic Acid.

This acid was isolated from the nitration of *o*-xylene-4-sulphonic acid in the form of its *amide* (see p. 1151). This was purified by crystallisation from alcohol, in which it is only sparingly soluble, and separates in large, prismatic needles, which melt at 214°. For analysis it was dried at 100°:

0.1058 gave 12.5 c.c.  $N_2$  at 33° and 763 mm.  $N=12.6$ .

$C_8H_9O_4N_2S$  requires  $N=12.2$  per cent.

In order to obtain the free acid, the amide (5 grams) was mixed with concentrated hydrochloric acid (15 c.c.), and heated in a sealed tube for four hours at 150–160°. The product was poured into water, filtered from a trace of carbonaceous matter, and evaporated to dryness on the water-bath, when a mixture of the nitro-sulphonic acid and ammonium chloride was obtained. To isolate the pure acid, the mixture was dissolved in water, and boiled with excess of baryta until no further odour of ammonia was perceptible, the barium exactly precipitated with sulphuric acid, and the filtered solution evaporated to dryness, when 3-nitro-*o*-xylene-4-sulphonic acid was obtained in needles, which, after crystallisation from a little water, were dried at 120° and analysed:

0.1317 gave 5.8 c.c.  $N_2$  at 30° and 763 mm.  $N=4.8$ .

$C_8H_9O_5NS, 3H_2O$  requires  $N=4.9$  per cent.

The barium salt crystallises in glistening, fatty-looking needles. For analysis it was dried at 130°:

0.2882 gave 0.1081  $BaSO_4$ .  $Ba=22.1$ .

$C_{16}H_{16}O_{10}N_2S_2Ba, H_2O$  requires  $Ba=22.3$  per cent.

*3-o-Nyldine-4-sulphonic Acid*.—This acid was prepared by the reduction of the corresponding nitro-acid by means of ferrous sulphate. It was purified by crystallisation from hot water, in which it is only very sparingly soluble, when it separated in octahedral prisms, which blacken but do not melt at 300°:

0.1122 gave 6.2 c.c.  $N_2$  at 29° and 765 mm.  $N=6.2$ .

$C_8H_{11}O_3NS_2H_2O$  requires  $N=6.4$  per cent.

The barium salt crystallises from water, in which it is sparingly soluble, in rectangular prisms possessing a high refractive index. It only slowly becomes pink on exposure to the air:

0.4471 lost 0.0249 at 120°.  $H_2O=5.6$ .

0.2437\* gave 0.104  $BaSO_4$ .  $Ba=25.1$ .

$C_{16}H_{20}O_6N_2S_2Ba_2 \cdot 2\frac{1}{2}H_2O$  requires  $H_2O=6.1$ .

$C_{16}H_{20}O_6N_2S_2Ba_2 \cdot 4H_2O$  „  $Ba=25.1$  per cent.

#### 4-Nitro-o-xylene-5-sulphonic Acid.

This acid was isolated in small quantities in the form of its amide from the nitration of o-xylene-4-sulphonic acid (see p. 1151). The amide crystallises from alcohol, in which it is somewhat readily soluble, in small, hard, prismatic needles, melting at 157—158°:

0.1117 gave 12.7 c.c.  $N_2$  at 33° and 763 mm.  $N=12.1$ .

$C_8H_{10}O_4N_2S$  requires  $N=12.2$  per cent.

4-Nitro-o-xylene-5-sulphonic acid was obtained from the amide by hydrolysis with hydrochloric acid, as was described above in the case of the 4-sulphonic acid, when it was isolated in bayonet-shaped, somewhat hygroscopic needles. As the amount at the disposal of the author was small, it was not further examined.

#### o-4-Nyldine-5-sulphonic Acid.

(1) From 4-Nitro-o-xylene-5-sulphonic Acid.—When this acid is reduced by means of alkaline ferrous sulphate, the amino-acid is readily isolated in the form of its barium salt.

The barium salt separates from hot water, in which it is readily soluble, in highly characteristic rectangular plates or spangles, which show straight extinction. It crystallises with eight molecules of water of crystallisation, which it loses at 125°:

0.2757 † gave 0.0944  $BaSO_4$ .  $Ba=20.1$ .

0.5638 lost 0.1154 at 125°.  $H_2O=20.4$ .

$C_{10}H_{20}O_6N_2S_2Ba_8 \cdot 8H_2O$  requires  $Ba=20.2$ ;  $H_2O=20.2$  per cent.

o-4-Nyldine-5-sulphonic acid crystallises in tablets which are only

\* Dried at 120°.

† Air dried.

very sparingly soluble in hot water. It blackens at  $280^{\circ}$ , but does not decompose at  $300^{\circ}$ . For analysis it was dried at  $120^{\circ}$ :

0.205 gave 0.243  $\text{BaSO}_4$ .  $\text{S}=16.3$ .

$\text{C}_8\text{H}_{11}\text{O}_3\text{NS}$  requires  $\text{S}=15.9$  per cent.

(2) *By the Sulphonation of o-4-Xylidine and s-Diaxylcarbimide* [ $\text{NH}:\text{Me}_2-1:3:4$ ].—When *o-4-xylidine* was sulphonated, as described on p. 1153, the highly characteristic barium salt of *o-4-xylidine-5-sulphonic acid* was readily separated from the reaction mixture. Careful examination both of the barium salt and the acid showed that it was identical with the acid obtained by the nitration of *o-xylene-4-sulphonic acid*.

This acid was also obtained when the above-mentioned carbimide was sulphonated (see p. 1153).

*Diazotisation of o-4-Xylidine-5-sulphonic Acid*.—In order to eliminate the amino-group and obtain *o-xylene-4-sulphonic acid*, the amino-sulphonic acid (prepared from *o-4-xylidine*) (0.2 gram) was dissolved in sulphuric acid (0.2 gram), and after the addition of a little alcohol (about 3 c.c.) amyl nitrite (5 c.c.) was added to the well-cooled solution. After an hour the mixture was heated on the water-bath, when the white solid which was suspended in the liquid passed into solution, and nitrogen was evolved. The product was poured into water, the sulphuric acid removed by means of barium carbonate, and the filtered solution evaporated on the water-bath, when the barium salt of *o-xylene-4-sulphonic acid* separated. This was converted into the amide in the usual manner; after crystallisation from alcohol the latter melted at  $143-144^{\circ}$ , and showed no depression when mixed with the amide of this acid obtained from another source.

#### *o-3-Xylidine-6-sulphonic Acid.*

This acid was obtained by the sulphonation of *o-3-xylidine* (see p. 1152) and was separated in the form of its barium salt; the latter is readily soluble in water, and crystallises in glistening, octahedral pyramids, which rapidly effloresce in the air. This salt also shows very markedly the property of supercooling:

0.3101 lost 0.0363.  $\text{H}_2\text{O}=11.7$ .

0.2738 gave 0.115  $\text{BaSO}_4$ .  $\text{Ba}=24.7$ .

$\text{C}_{16}\text{H}_{20}\text{O}_6\text{N}_2\text{S}_2\text{Ba}\cdot\text{H}_2\text{O}$  requires  $\text{Ba}=24.7$ .

Loss of  $4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=11.5$  per cent.

*o-3-Xylidine-6-sulphonic acid* separates from water in bunches of sheaf-like needles, which do not change colour in the air. It does not darken when heated to  $305^{\circ}$ :

0.1195 gave 7.3 c.c.  $\text{N}_2$  at  $28^{\circ}$  and 763 mm.  $\text{N}=6.7$ .

$\text{C}_8\text{H}_{11}\text{O}_3\text{NS}$  requires  $\text{N}=7.0$  per cent.

*o*-4-Xylidine-6-sulphonic Acid (?).

This acid was separated in the form of its sparingly soluble barium salt from the sulphonation of *o*-4-xylidine and of *s*-dixylyl-carbamide (see p. 1153). The *barium* salt separates from hot water in large, well-developed plates, belonging probably to the orthorhombic system, the corner angle measuring approximately 90°. The crystals, on exposure to the air, slowly become pink. For analysis the salt was dried at 120°, when no loss of weight occurred:

0.228 gave 0.0946 BaSO<sub>4</sub>. Ba = 24.3.

C<sub>10</sub>H<sub>20</sub>O<sub>6</sub>N<sub>2</sub>S<sub>2</sub>Ba, 1½H<sub>2</sub>O requires Ba = 24.3 per cent.

*o*-4-Xylidine-6-sulphonic acid, obtained from the barium salt, crystallises from hot water in aggregates of plates, which do not easily rodden in the air. When heated in a capillary tube it darkens at 283°, and melts and decomposes at 294°. It apparently contains two molecules of water of crystallisation, which it does not lose at 120°:

0.1634 gave 0.1653 BaSO<sub>4</sub>. S = 13.9.

C<sub>8</sub>H<sub>11</sub>O<sub>8</sub>NS, 2H<sub>2</sub>O requires S = 13.7 per cent.

When the acid is diazotised with barium nitrite, and the diazo-compound boiled with water, the xylenolsulphonic acid was obtained in prismatic needles, which gave a bright blue coloration with ferric chloride. An attempt was made to fuse it with potassium hydroxide in order to isolate the dihydroxyxylene, but no satisfactory result was obtained. The trace of dihydroxyxylene that was isolated gave a purple coloration with ferric chloride, but it was too small in quantity for further examination.

*Nitration of o-Xylene-4-sulphonic Acid.*

In carrying out the nitration of *o*-xylene-1-sulphonic acid, the following method was found to give the most satisfactory results. Fuming nitric acid (D 1.5) (255 grams) was well cooled in a freezing mixture, and the sulphonic acid (85 grams) was gradually added with constant shaking. The sulphonic acid slowly passed into solution, and after remaining in ice for six hours, the mixture was allowed to remain at the room temperature (30°) for two days, and then poured into a large volume of water. A flocculent precipitate (2.5 grams) separated; this was collected and reserved for further examination (see below).

In order to isolate the nitro-sulphonic acids, the acid liquor was evaporated as far as possible under diminished pressure on the water-bath, the last traces of nitric acid being removed over



potassium hydroxide in a vacuum desiccator. The semi solid mass thus obtained was dissolved in water and treated with barium hydroxide, the excess of barium hydroxide removed by carbon dioxide, and the pale yellow solution of the barium salts was concentrated on the water-bath, when the sparingly soluble barium salt of 3-nitro-*o*-xylene-5-sulphonic acid separated in prismatic needles (yield 34 grams). On concentrating the mother liquor, a second crop of the same substance was obtained.

Since the filtrate on further concentration yielded no definitely crystalline product, the mixture of barium salts (85 grams) was carefully dried, and, after mixing with excess of phosphorus pentachloride, heated on the water-bath for an hour. On decomposing the mixture with ice-water, the acid chloride (64 grams) separated as an oil, which was isolated by means of ether, dried, and without further purification converted into the amide with ammonium carbonate. The crude, brown amide obtained in this way was subjected to a careful process of fractional crystallisation from alcohol, when it was separated into two main fractions: (*a*) a very sparingly soluble amide melting at  $214^{\circ}$  (15 grams), the amide of 3-nitro-*o*-xylene-4-sulphonic acid, and (*b*) a more readily soluble amide melting at  $157-158^{\circ}$  (2.8 grams), the amide of 4-nitro-*o*-xylene-5-sulphonic acid. The mother liquors contained a mixture of amides (18 grams), which could not be purified.

It was mentioned above that when the nitration products were poured into water a small quantity of an insoluble substance separated. This was crystallised from benzene, from which it separated in yellow leaflets resembling picric acid. When heated fairly rapidly, it sinters at  $170^{\circ}$ , and melts and decomposes at  $183-185^{\circ}$ :

0.1307 gave 17.8 c.c.  $N_2$  at  $28^{\circ}$  and 759 mm.  $N=14.8$ .

$C_8H_6O_4N_2$  requires  $N=14.3$  per cent.

This new *dinitro-o-xylene*, which must contain one of the nitro-groups in the side-chain, is readily soluble in alcohol, but is precipitated from it as an oil, from which the original substance could not be isolated. It is soluble in sodium carbonate, and is not reprecipitated on acidification. Further experiments are in progress with the view of elucidating the constitution of this substance.

#### *Sulphonation of o-3-Xylidine.*

*o*-3-Xylidine (12 grams) was mixed with sulphuric acid (36 c.c.), and heated for two hours at  $160^{\circ}$ , and finally at  $180^{\circ}$  for one hour. The brown product was cooled and poured into water, when a large amount of solid (10 grams) separated, and was collected. The

filtrate was carefully examined, but no pure substance could be isolated.

For the purposes of purification, the above-mentioned solid was converted into its barium salt, and subjected to a long process of crystallisation. It was found to consist of a mixture of the barium salts of *o*-3-xylylidine-6-sulphonic acid (3 grams) and *o*-3-xylylidine-5-sulphonic acid (6 grams). Indications of the presence of a third salt were obtained, but it could not be isolated in sufficient quantity for purification.

*Sulphonation of o-4-Xylylidine.*

*o*-4-Xylylidine was sulphonated under similar experimental conditions to those just described. On pouring the product into water, a voluminous, white precipitate separated (8 grams). This was collected, and the filtrate was found to contain a small quantity of *o*-4-xylylidine-5-sulphonic acid.

In order to separate the sparingly soluble mixture of sulphonic acids, recourse was again had to the difference in solubility of the barium salts. On allowing a dilute solution to remain, it slowly deposits the barium salt of *o*-4-xylylidine-6-sulphonic acid in large, rectangular plates, some of them more than 4 mm. in size (yield 3 grams). The mother liquor from which this barium salt separated was concentrated, when the barium salt of *o*-4-xylylidine-5-sulphonic acid was obtained in beautiful spangles (7 grams).

*Sulphonation of s-Diarylcyanamide (NH: Me<sub>2</sub> = 1 : 3 : 4).*

The cyanamide (2.5 grams) was mixed with sulphuric acid (10 c.c.), and heated at 160° until all evolution of carbon dioxide had ceased (compare *Bull. Soc. chim.*, 1896, [iii], 19, 21). The product was examined as has been described above, and was found to consist of a mixture of *o*-4-xylylidine-5-sulphonic acid and *o*-4-xylylidine-6-sulphonic acid, the former acid predominating.

The author wishes to thank the Research Fund Committee for a grant which defrayed part of the expense of this investigation.

THE PRESIDENCY COLLEGE,  
MADRAS.

CXXI.—*The Relative Activities of Certain Organic Iodo-compounds with Sodium Phenoxide in Alcoholic Solution. Part I. Some Normal Primary Alkyl Iodides.*

By DAVID SEGALLER.

DURING the past few decades a considerable amount of research has been undertaken with the object of determining the relative reactivities of various organic substances, and there can be little doubt that the results obtained will have a powerful influence on the development of future theories of chemical reactivity. In general, reaction between organic compounds is much more complex than that which takes place between inorganic substances, so that it is necessary to deal only with the simplest forms of reaction when studying the reactivities of organic compounds. Among such reactions are those which take place between organic iodides and sodium derivatives of alcohols and phenols, and a certain amount of work has already been done in this direction by Hecht, Conrad, and Bruckner (*Zeitsch. physikal. Chem.*, 1899, **4**, 273), Menschutkin (*ibid.*, 1890, **5**, 589), Brinsoff (*ibid.*, 1900, **34**, 129). A valuable summary of these results is given by Burke and Donnan (*T.*, 1904, **85**, 555), who investigated the reactivities of some alkyl iodides with silver nitrate. The results obtained by the latter authors do not agree with those found by some of the other investigators, for example, Hecht, Conrad, and Bruckner (*ibid.*), and Menschutkin (*ibid.*). It might here be pointed out that in Burke and Donnan's reaction mixture silver iodide was precipitated, and the change of phase so produced may possibly have influenced the velocity of the reaction. Conrad and Bruckner, in continuation of their investigation on the velocity of ether formation (*Zeitsch. physikal. Chem.*, 1891, **7**, 274), made a few measurements of velocity-constants, in which the reaction mixture consisted of alkyl iodide (they measured only methyl, ethyl, and propyl iodides), sodium ethoxide, and phenol. Measurements of the reactivities of some organic halogen compounds have also been made by Slator (*T.*, 1904, **85**, 1286), who used sodium thiosulphate. Preston and Jones (*T.*, 1912, **101**, 1930) measured the rates of reaction of methyl, ethyl, propyl, and allyl iodides with certain tertiary bases, and found some anomaly in the behaviour of methyl iodide.

The author of the present communication considered it desirable to undertake a more extended study of the reactivities of the organic iodides than any yet recorded, and for the purposes of this

investigation sodium phenoxide was selected as the reagent with which the relative reactivities were to be measured. The sodium phenoxide was prepared by a modification of Forcrand's method (*Ann. Chim. Phys.*, 1893, [vi], 30, 60). Considerable difficulty was encountered in obtaining the substance in a sufficient state of purity, the only satisfactory process being to prepare it as directed by Forcrand, then to crystallise it from methyl alcohol or acetone, and to heat the product in a current of pure dry hydrogen for some hours at about 150°. The substance prepared in this manner is quite colourless. (Found, Na=19.78, 19.73. Calc., Na=19.82 per cent.)

The following table and curve (Fig. 1) show the relative reactivities of those primary normal alkyl iodides measured by Menschutkin, Hecht, and Conrad, and Burke and Donnan:

	Menschutkin.	Hecht and Conrad.	Burke and Donnan.
Methyl .....	11.40	61.72	1.35
Ethyl .....	10.1	4.87	3.25
Propyl .....	1.43	1.71	1.52
Butyl .....	1.38	—	1.00
Amyl .....	—	—	—
Hexyl .....	—	—	—
Heptyl .....	1.38	1.04	—
Octyl .....	1.08	1.00	—

The present communication deals only with the normal primary alkyl iodides, the results obtained with the secondary and tertiary alkyl iodides being reserved for a future paper.

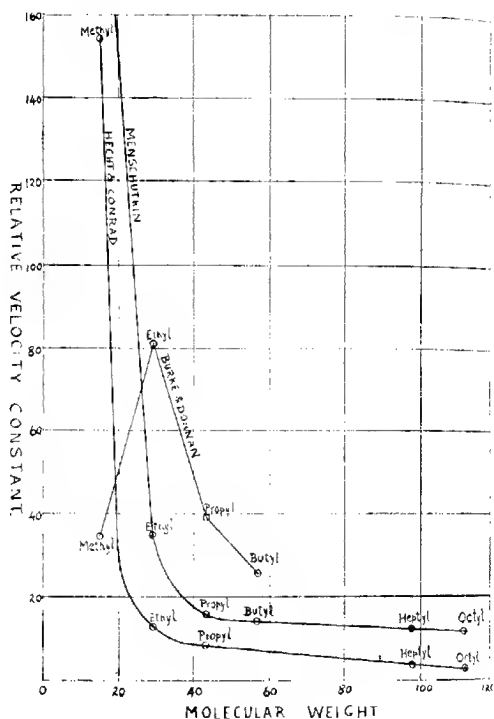
The alcohol used was the commercial "absolute," which was twice distilled from fresh quicklime. It was then boiled under reflux with metallic calcium turnings for some hours, and finally distilled from the calcium into bottles provided with drying tubes.

The iodides used were in most cases Kalilbaum's preparations, whilst the normal hexyl and heptyl iodides were prepared by the author by standard methods. The purification of these iodides was generally carried out as follows: The substance was washed with dilute sodium hydroxide, then with water, and finally dried over calcium chloride in the usual way, and fractionated. In many cases (especially with the higher homologues) it is not possible to obtain a colourless liquid in this way, even when fractionation is done in a vacuum. To free the substance completely from dissolved iodine the liquid was shaken with freshly ignited silver powder. In this way a quite colourless product of correct boiling point was obtained in every instance, and was immediately used for the reaction. It was found that after the iodide had been thoroughly purified in this manner, the best way to preserve it was to keep a little silver powder in the bottle containing the liquid. Some

isopropyl iodide (which, as is well known, becomes coloured with great rapidity even out of contact with air and in the dark), so purified and preserved by the author, was found after two years, to be quite colourless and of correct boiling point.

To prevent evaporation in the thermostat, the water was covered

FIG. 1.



with a layer of lubricating oil. It might not be out of place to mention a slight improvement in the thermo-regulator, which was of a modified Ostwald type and kept the temperature of the bath constant to  $1/50^{\circ}$ . The side-tube containing the micrometer screw was inclined downwards instead of being in the usual horizontal position, and in this way the tendency for tiny air bubbles to be

sucked in was avoided, beside having the advantage that if the bath has to be cooled and re-heated, the side-tube becomes completely filled with mercury before the latter rises further in the capillary. This is not always the case with regulators where the manometer screw is at right angles to the stem.

The thermometers and all measuring vessels used were "Standard."

The measurements of the velocity-coefficients were carried out as follows: Solutions of known strength (generally  $N$ ) of the iodide under consideration and the sodium phenoxide, both in absolute ethyl alcohol, were prepared. Of each of these solutions 50 c.c. were transferred into a stoppered Jena-glass bottle, which was then thoroughly shaken, and 10 c.c. of this mixture transferred into each of eight Jena glass test-tubes, which were immediately tightly stoppered with rubber corks. The test-tubes fitted into a brass stand, which was lowered so as to rest on a tray in the bath, the tubes being almost completely immersed. After the mixture had attained the temperature of the bath (generally in fifteen minutes), the time was noted, and a test-tube rapidly taken out and emptied into a beaker containing some ice and an amount of  $N/20$ -hydrochloric acid almost sufficient to neutralise any unchanged sodium phenoxide (this was ascertained by a parallel experiment). Phenolphthalein was then added, and the neutralisation completed from a burette. This was taken as the "zero" of the measurements. After various intervals of time, varying according to the reactivity of the substance used, other test-tubes were dealt with in this way. The velocity-constant was calculated according to the usual formula for a bimolecular reaction.

$t$  = time in minutes.

$a$  = concentration of sodium phenoxide.

$b$  = " " alkyl iodide in gram molecules.

$x$  = amount of sodium phenoxide changed in time  $t$ .

$K$  = velocity-constant.

In the following experiments the initial concentrations were

equal, so that  $a = b$  and  $K = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

so that if  $a$  = number of c.c. of acid required to neutralise the mixture at the zero,

$a - x$  = number of c.c. of acid required to neutralise the mixture after time  $t$ .

Then since  $a$  and  $(a - x)$  are proportional to the concentrations of the sodium phenoxide at times 0 and  $t$  respectively, if

$y$  = number of c.c. of the acid being used at the time which would be required to neutralise the

amount of sodium phenoxide contained by each mixture before commencement of experiment.

$$\text{then } K = \frac{1}{t} \cdot \frac{x}{(a-x)} \cdot \frac{y}{a},$$

$$\text{let } k = \frac{1}{t} \cdot \frac{x}{a-x},$$

$$\text{then } K = k \cdot \frac{y}{a}.$$

All the following experiments were carried out at 42.5°.

### *Methyl Iodide.*

Each mixture contained 5 c.c. of *N*-methyl iodide and 5 c.c. of *N*-sodium phenoxide. The acid used was *N*/5-hydrochloric acid, therefore  $y=25$ .

#### I.

Zero = 22.40 c.c.

<i>t</i> .	<i>a-x</i> .	<i>x</i> .	<i>k</i> .
10	17.16	5.24	0.03054
15	15.44	6.96	0.03001
20	13.95	8.45	0.03029
25	12.90	9.50	0.02945
30	11.76	10.64	0.03016
35	10.88	11.52	0.03025

$$k \text{ mean} = 0.03012$$

$$\therefore K = k \times 25/22.4 = 0.03362$$

#### II.

Zero = 20.80 c.c.

<i>t</i> .	<i>a-x</i> .	<i>x</i> .	<i>k</i> .
10	16.23	4.57	0.02815
15	14.65	6.15	0.02801
20	13.35	7.45	0.02791
25	12.30	8.50	0.02764
30	11.38	9.42	0.02751
40	9.85	10.95	0.02789

$$k \text{ mean} = 0.02784$$

$$K = k \times 25/20.8 = 0.03258$$

Another experiment in which *N*/2-solutions were used gave  $K=0.03514$ . Further investigation, however, showed that comparable results can only be obtained if the initial concentrations are the same for all substances under comparison.

In this investigation *N*-solutions were therefore used throughout.

In the following tables full data are given only for one experiment, and the mean coefficient for another experiment. In the case of *n*-heptyl iodide material from two different sources was used and in this case data for both experiments are given.

### *Ethyl Iodide.*

This was purified as above. Each mixture contained 5 c.c. of *N*-ethyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5;  $y=25$ .

## I.

Zero=21.80 c.c.

$t_s$	$\alpha - \beta$	$\beta$	$k$
60	15.90	5.90	0.006184
90	14.00	7.80	0.006190
120	12.60	9.20	0.006085
150	11.30	10.50	0.006194
180	10.40	11.40	0.006080

$$k \text{ mean} = 0.006124$$

$$K = k \times 25/21.8 = 0.007023$$

## II.

$$K \text{ mean} = 0.007003$$

*n-Propyl Iodide.*

This was purified as above. Each mixture consisted of 5 c.c. of *n*-propyl iodide and 5 c.c. of *N*-sodium phenoxide. The acid used was 1.108*N* 45-hydrochloric acid, therefore  $\mu = 27.7$ .

## I.

Zero=22.45 c.c.

$t_s$	$\alpha - \beta$	$\beta$	$k$
45	20.40	2.05	0.002233
90	18.65	3.80	0.002264
120	17.80	4.85	0.002296
215	15.20	7.25	0.002219
240	14.52	7.93	0.002274

$$k \text{ mean} = 0.002257$$

$$K = k \times 27.7/22.45 = 0.002788$$

## II.

$$K \text{ mean} = 0.002800$$

*n-Butyl Iodide.*

This was purified as above. Each mixture consisted of 5 c.c. of *n*-butyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid= $N/5$ ;  $\mu = 25$ .

## I.

Zero=23.90 c.c.

$t_s$	$\alpha - \beta$	$\beta$	$k$
60	19.50	4.40	0.002504
210	15.72	8.18	0.002478
270	14.48	9.42	0.002409
330	13.30	10.60	0.002416
340	10.70	13.20	0.002410

$$k \text{ mean} = 0.002411$$

$$K = k \times 25/23.9 = 0.002544$$

## II.

$$K \text{ mean} = 0.002566$$



*n-Amyl Iodide.*

The substance was purified by shaking with freshly ignited silver powder just before use. It was then quite colourless, <sup>higher</sup> and boiled at 156° (corr.).

On account of its costly nature, the mixtures in this case consisted of only 2 c.c., composed of a mixture of equal volumes of *N*-amyl iodide and *N*-sodium phenoxide. The acid was *N*-10-hydrochloric acid, therefore  $y=10$ .

## I.

Zero = 9.40 c.c.

$t$ ,	$u-x$ ,	$x$ ,	$k$ ,
100	8.46	0.94	0.001111
200	7.74	1.66	0.001072
300	7.13	2.27	0.001061
400	6.56	2.84	0.001082
500	6.13	3.27	0.001067
600	5.72	3.68	0.001073

$$k \text{ mean} = 0.001078$$

$$K = k \times 10/9.4 = 0.001117$$

## II.

$$K \text{ mean} = 0.001126$$

*n*-Amyl iodide gives much lower results than would have been expected.

*n-Hexyl Iodide.*

The substance was colourless and boiled at 180°.

Each mixture consisted of 5 c.c. of *N*-hexyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5;  $y=25$ .

## I.

Zero = 24.25 c.c.

$t$ ,	$u-x$ ,	$x$ ,	$k$ ,
80	20.35	3.90	0.002396
180	17.02	7.23	0.002356
240	15.38	8.87	0.002406
300	14.20	10.05	0.002359
400	12.55	11.70	0.002330
500	11.20	13.05	0.002336

$$k \text{ mean} = 0.002362$$

$$K = k \times 25/24.25 = 0.002436$$

## II.

$$K \text{ mean} = 0.002438$$

*n-Heptyl Iodide.*

The substance was purified as above. It was quite colourless, and boiled at 204°.

Each mixture contained 5 c.c. of *N*-heptyl iodide and 5 c.c. of sodium phenoxide. The acid was  $N/10$ ;  $y=50$ .

## I.

Zero = 47.60 c.c.

<i>t</i> .	$\alpha-x$ .	$x$ .	<i>k</i> .
165	38.32	9.28	0.002306
225	31.50	16.10	0.002272
285	28.85	18.25	0.002285
345	26.50	21.10	0.002309
495	22.30	25.30	0.002289

$$k \text{ mean} = 0.002292$$

$$K = k \times 50/47.6 = 0.002108$$

## II.

A different preparation gave the following results.

Acid =  $N/5$ ;  $y=25$ .

Zero = 23.85 c.c.

<i>t</i> .	$\alpha-x$ .	$x$ .	<i>k</i> .
100	19.33	4.52	0.002338
200	16.24	7.61	0.002342
300	14.03	9.82	0.002333
400	12.42	11.43	0.002300
500	11.14	12.71	0.002281
600	9.95	13.90	0.002327

$$k \text{ mean} = 0.002320$$

$$K = k \times 25/23.85 = 0.002452$$

*n-Octyl Iodide.*

The substance was purified as described above.

Each tube contained 5 c.c. of *N*-octyl iodide and 5 c.c. of sodium phenoxide. The acid was  $N/10$ ;  $y=50$ .

## I.

Zero = 47.50 c.c.

<i>t</i> .	$\alpha-x$ .	$x$ .	<i>k</i> .
110	38.00	9.50	0.002220
214	32.25	15.25	0.002251
250	29.25	18.25	0.002229
340	26.75	20.75	0.002281
500	22.10	25.40	0.002298
600	22.00	27.50	0.002291

$$k \text{ mean} = 0.002270$$

$$K = k \times 50/47.5 = 0.002389$$

## II.

$$K \text{ mean} = 0.002382$$

*Cetyl Iodide.*

The substance was purified by repeated crystallisation from alcohol, and dried in a vacuum. It then consisted of white, pearly scales, melting at  $22^{\circ}$ , and boiling at  $212^{\circ}/745$  mm.

Each mixture contained 5 c.c. of *N*-cetyl iodide and 5 c.c. of sodium phenoxide. The acid was  $N/5$ ;  $y=25$ .

## I.

Zero = 24.20 c.c.

<i>t</i> .	$\alpha - x$ .	<i>x</i> .	<i>k</i> .
80	20.73	3.47	0.002092
120	19.37	4.83	0.002077
330	14.95	9.25	0.002062
400	13.24	10.96	0.002069
500	11.43	12.27	0.002056
600	10.80	13.40	0.002070
			$k$ mean = 0.002071
			$K = k \times 25/24.2 = 0.002140$

## II.

$K$  mean = 0.002185

The following numbers and curve (Fig. 2) express the relative reactivities of the substances dealt with in this paper, as measured by sodium phenoxide in alcoholic solution:

Methyl .....	14.63	<i>n</i> -Hexyl .....	1.08
Ethyl .....	3.03	<i>n</i> -Heptyl .....	1.05
<i>n</i> -Propyl .....	1.21	<i>n</i> -Octyl .....	1.01
<i>n</i> -Butyl .....	1.15	<i>n</i> -Cetyl .....	1.00
<i>n</i> -Amyl .....	0.49		

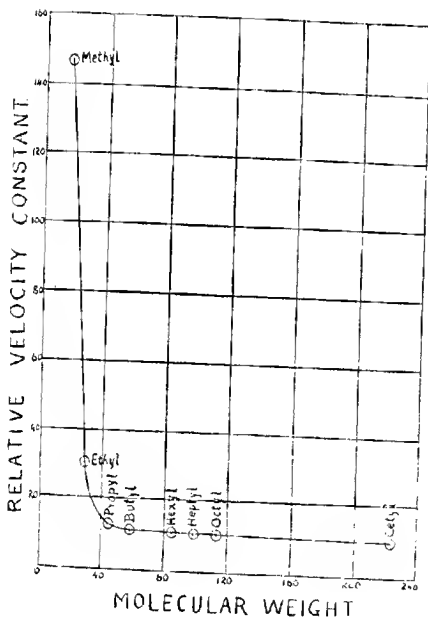
When  $M/K$  is plotted against  $M$ , the graph below (Fig. 3) is obtained. The deviation, however, from the rectilinear relation is greater than at first sight, owing to the relatively large variation of  $M/K$  with  $M$ . The greatest deviations appear in the cases of ethyl and amyl iodides, the latter lying quite off the line in the diagram.

*The Effect of Initial Concentration on the Velocity-coefficient.*

As mentioned above, it was found that comparable results could be obtained only when the initial concentration of each reaction mixture was the same in each case, and for that reason the experiments described have dealt only with solutions the initial concentrations of which were kept normal.

This effect of initial concentration on the magnitude of the velocity-coefficient is a point of great importance, and does not seem to have been investigated in a large number of reactions in which velocity of reactions has been studied. Hecht and Conrad, in their work on the rate of ether formation (*loc. cit.*), found that a decrease in concentration of the sodium ethoxide raised the velocity-coefficient, but that a decrease in the concentration of the

FIG. 2.



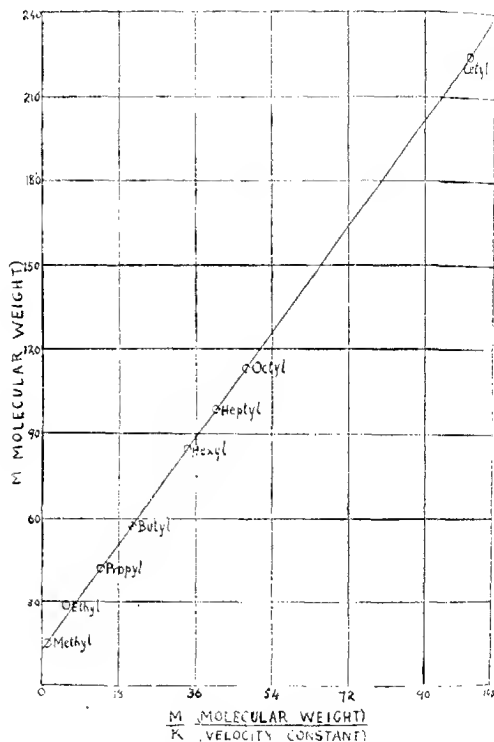
alkyl iodide had very little effect in that direction. These authors also found that their results could be connected fairly well by the formula  $K_r = K_1 + a \log r$ , where  $a$  is a constant, and  $r$  the reciprocal of the initial equivalent concentration.

Burke and Donnan (*loc. cit.*) found that a decrease in the concentration of the alkyl iodide raised the velocity-coefficient, but that this was diminished by a decrease in the concentration of the silver nitrate. Sator (*loc. cit.*), on the other hand, does not find

any appreciable alteration in the velocity-coefficient by change in the initial concentration.

With the object of obtaining more information on this subject, some measurements were made of the velocity-coefficient, using

FIG. 3.



solutions of *n*-propyl iodide and of sodium phenoxide less and greater than normal. The experiments fall into three groups:

(A) The initial concentrations of both the phenoxide and the iodide altered, but using equivalent initial concentrations.

(B) The initial concentration of the iodide kept at normal, but that of the phenoxide altered.

(C) The initial concentration of the phenoxide kept at normal, but that of the iodide altered.

In the cases of *B* and *C*, the velocity-coefficient was calculated by means of the equation:

$$K = \frac{1}{(a-b)t} \cdot \log_e \frac{(a-x)b}{(b-x)a},$$

where *a*, *b*, *c* have the same significance as above.

#### A.

Each mixture contained 10 c.c. of *N*/2 propyl iodide and 5 c.c. of *N*/2-sodium phenoxide. The acid was *N*/10.

Zero = 23.64 c.c.

<i>t</i> .	<i>a - x</i> .	<i>x</i> .	<i>K</i> .
100	19.99	3.61	0.003616
200	17.29	6.31	0.003648
300	15.47	8.13	0.003704
400	14.05	9.55	0.003490
500	12.72	10.88	0.003420
600	11.69	12.00	0.003448

*K* mean = 0.003506

Each mixture contained 10 c.c. of *N*/5-propyl iodide and 10 c.c. of *N*/5-sodium phenoxide. The acid was *N*/10.

Zero = 18.60 c.c.

<i>t</i> .	<i>a - x</i> .	<i>x</i> .	<i>K</i> .
100	17.16	1.44	0.004193
250	15.48	3.12	0.004031
405	14.00	4.66	0.004074
465	13.06	5.24	0.004217
650	13.00	5.60	0.004026
791	11.82	6.78	0.004092

*K* mean = 0.004115

Each mixture contained 10 c.c. of *N*/10-propyl iodide and 10 c.c. of *N*/10-sodium phenoxide. The acid was *N*/20.

Zero = 18.20 c.c.

<i>t</i> .	<i>a - x</i> .	<i>x</i> .	<i>K</i> .
300	15.94	2.26	0.005197
400	15.26	2.94	0.005281
600	14.20	4.00	0.005164
800	13.22	4.98	0.005174
1000	12.38	5.82	0.005166
1200	11.62	6.58	0.005182

*K* mean = 0.005196

VOL. CIII.

As shown in the following table, the above results are fairly well represented by Hecht and Conrad's equation:  $K_s = K_1 + a \log r$ :

Concentration of sodium phenoxide.	Concentration of <i>n</i> -propyl iodide.	$K$ (found.)	$K_s = K_1 + a \log r$ , $a = 0.002299$ .
$N$	$N$	0.002800	0.002899
$N/2$	$N/2$	0.003506	0.003498
$N/5$	$N/5$	0.004415	0.004413
$N/10$	$N/10$	0.005196	0.005105

## B.

Each mixture contained 5 c.c. of *N*-propyl iodide and 5 c.c. of  $N/2$ -sodium phenoxide. Acid =  $N/10$ .

$t$ .	$a - x$ .	$b - x$ .	$K$ .
0	23.10	48.10	—
30	19.12	44.12	0.002427
80	17.35	42.35	0.003526
125	16.02	41.02	0.003309
180	13.74	38.74	0.003392
240	11.84	36.81	0.003426
360	10.18	35.18	0.003376

$K$  mean = 0.003409

Each mixture contained 10 c.c. of *N*-propyl iodide and 10 c.c. of  $N/5$ -sodium phenoxide. Acid =  $N/10$ .

$t$ .	$a - x$ .	$b - x$ .	$K$ .
0	17.83	97.83	—
30	15.70	95.70	0.004421
50	14.50	94.50	0.004285
70	13.40	93.40	0.004267
100	11.97	91.97	0.004203
120	11.15	91.15	0.004150
150	9.68	89.68	0.004361

$K$  mean = 0.004283

Each mixture contained 20 c.c. of *N*-propyl iodide and 20 c.c. of  $N/10$ -sodium phenoxide. Acid =  $N/10$ .

$t$ .	$a - x$ .	$b - x$ .	$K$ .
0	18.20	198.20	—
20	16.50	196.50	0.005098
30	15.61	195.61	0.005205
50	14.28	194.28	0.004942
67	13.15	193.15	0.004957
81	12.20	192.20	0.005071
125	10.12	190.12	0.004849

$K$  mean = 0.005019

Concentration of sodium phenoxide.	Concentration of <i>n</i> -propyl iodide.	$K$ (found.)	$K_s = K_1 + a \log r$ , $a = 0.002122$ .
$N$	$N$	0.002800	0.002809
$N/2$	$N$	0.003409	0.003415
$N/5$	$N$	0.004283	0.004288
$N/10$	$N$	0.005019	0.004928

## C.

Each mixture contained 5 c.c. of 4*N*-propyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5.

<i>t</i> .	<i>a</i> - <i>x</i> .	<i>b</i> - <i>x</i> .	<i>K</i> .
0	20.70	95.70	—
30	15.92	90.92	0.002400
60	12.17	87.17	0.002430
75	10.84	85.84	0.002390
85	9.90	84.90	0.002421
95	9.00	84.00	0.002462
100	7.97	82.97	0.002152

$$K \text{ mean} = 0.002426$$

Each mixture contained 5 c.c. of 2*N*-propyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5.

<i>t</i> .	<i>a</i> - <i>x</i> .	<i>b</i> - <i>x</i> .	<i>K</i> .
0	22.18	47.18	—
60	16.45	41.45	0.002802
90	14.26	39.26	0.002862
120	12.62	37.62	0.002908
174	10.82	35.82	0.002568
220	8.82	33.82	0.002678
250	8.12	33.12	0.002600

$$K \text{ mean} = 0.002708$$

Each mixture contained 5 c.c. of *N*,2-propyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5.

<i>t</i> .	<i>a</i> - <i>x</i> .	<i>b</i> - <i>x</i> .	<i>K</i> .
0	23.46	10.96	—
44	22.20	9.70	0.003042
150	20.06	7.56	0.002806
200	18.20	5.70	0.003073
320	16.55	4.05	0.003071
485	16.13	3.63	0.003010
564	15.70	3.20	0.002946

$$K \text{ mean} = 0.002960$$

Each mixture contained 5 c.c. of *N*,5-propyl iodide and 5 c.c. of *N*-sodium phenoxide. Acid = *N*/5.

<i>t</i> .	<i>a</i> - <i>x</i> .	<i>b</i> - <i>x</i> .	<i>K</i> .
0	24.40	4.40	—
56	23.60	3.60	0.003732
110	23.02	3.02	0.003610
150	22.58	2.58	0.003799
230	22.05	2.05	0.003596
250	21.84	1.84	0.003669
450	20.78	0.78	0.003617

$$K \text{ mean} = 0.003670$$



Concentration of sodium phenoxide.	Concentration of n-propyl iodide.	$K$ (found.)	$K_e = K_1 + a \log c$ $a = 0.0069$ .
$N$	$4N$	0.002426	0.002338
$N$	$2N$	0.002708	0.002609
$N$	$N$	0.002800	0.002830
$N$	$N/2$	0.002990	0.003151
$N$	$N/5$	0.003670	0.003509

Although the equation used in the tables above answers well, the results can be represented even more satisfactorily by an equation of the type:  $K = p + q/c$ , where  $p$  and  $q$  are constants independent of the concentration  $c$ . In the relation between the velocity-coefficient and the initial concentration, where the phenoxide is kept at constant initial concentration and that of the iodide varied, then  $p = 0.00258$  and  $q = 0.000218$ .

Concentration of n-propyl iodide.	$K$ (found.)	$K = p + q/c$ .
$4N$	0.002426	0.002634
$2N$	0.002708	0.002889
$N$	0.002800	0.002788
$N/2$	0.002990	0.003016
$N/5$	0.003670	0.003670

*Mean Velocity-coefficients for n-Propyl Iodide and Sodium Phenoxide.*

Concentration of sodium phenoxide.	Concentration of n-propyl iodide.	Mean value of $K$ .	$K_e = K_1 + a \log c$ .
$N$	$N$	0.002800	0.002806
$N$	$4N$	0.002426	0.002333
$N$	$2N$	0.002708	0.002609
$N$	$N/2$	0.002990	0.003151
$N$	$N/5$	0.003670	0.003509
$N/2$	$N/2$	0.003506	0.003493
$N/2$	$N$	0.003409	0.003445
$N/5$	$N/5$	0.004115	0.004113
$N/5$	$N$	0.004253	0.004289
$N/10$	$N/10$	0.005196	0.005105
$N/10$	$N$	0.005019	0.004925

The above table brings out the following facts:

(1) An increase in the initial concentration of either the phenoxide or the iodide produces a decrease in the value of  $K$ , whereas a decrease in the initial concentration of either the phenoxide or the iodide produces an increase in the value of  $K$ . This differs from the results of Hecht and Conrad, who found that only a decrease in the concentration of the ethoxide produces any considerable increase in the value of  $K$ .

Burke and Donnan, on the other hand, find a decrease in  $K$  with decrease in concentration of the silver nitrate.

(2) The initial concentration of the phenoxide exerts a much greater influence on the reaction-velocity than that of the iodide. In the case of change of concentration of the phenoxide, the

constant  $a$  in the above equations is 0.002299, whereas by change of concentration of the iodide only,  $a=0.0009$ , and, as was to be expected from these facts, the value of  $a$  when the concentrations of both the phenoxide and the iodide were changed is equal to 0.002122, that is, lies between 0.002299 and 0.0009.

(3) The connexion between the velocity-coefficient and the initial concentration can be well expressed by the equation  $K_v = K_1 + a \log v$ , or by an equation of the type  $K = p + q/c$ .

#### General Conclusions.

(1) The reaction between the alkyl iodides and sodium phenoxide in alcoholic solution is a bimolecular one of a special type, in which the velocity-coefficient varies with the initial concentration.

(2) The reactivities of the normal primary alkyl iodides with sodium phenoxide are in the following decreasing order of magnitude: methyl, ethyl, propyl, butyl, hexyl, heptyl, octyl, cetyl, and amyl iodides.

(3) The velocity-coefficients lie on a curve (with the exception of amyl iodide), which is very steep from methyl to butyl iodide, and is then very shallow, the velocity-coefficient of cetyl iodide not being much less than that of octyl iodide.

(4) In the cases of those iodides which have been previously investigated, the relative order of the reactivities found by the author agrees with that obtained by some other investigators, for example, Hecht, Conrad, and Bruckner (*loc. cit.*), who used sodium ethoxide, and Menschutkin, who employed triethylamine in acetone solution, but does not agree with that found by Burko and Donnan, whose reagent was silver nitrate.

(5) The relative reactivity of amyl iodide is unexpected. The velocity-coefficient of this substance has not previously been determined, and repeated measurements by the author confirm its comparative inactivity. An explanation which might be suggested is that a cyclic compound is formed with the elimination of hydrogen iodide. It is interesting to notice that a parallel case was observed by Crocker (T., 1907, 91, 593) in an investigation on the velocity of hydrolysis of the aliphatic amides, in which he found the velocity-constant of valeramide to be the smallest of the series.

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CXXII.—*Rate of Evolution of Gases from Supersaturated Solutions. Part I. Influence of Colloids and of Suspensions of Charcoal on the Evolution of Carbon Dioxide.*

By ALEXANDER FINDLAY and GEORGE KING (Priestley Research Scholar, University of Birmingham).

IN the course of investigations of the influence of colloids on the solubility of gases (Findlay and Creighton, T., 1910, **97**, 536; Findlay and Shen, *ibid.*, 1912, **101**, 1459), marked differences were observed in the rate of escape of gas from supersaturated solutions. It was therefore deemed to be of interest to study the matter more fully, not only on account of the light which such investigations might throw on the properties of colloidal solutions, but also on account of its importance in connexion with biological problems (respiration, etc.) and industrial operations, such as the manufacture and the properties of mineral waters and other aerated beverages. In the present communication an account is given of the apparatus employed, the method of working, and the chief results so far obtained.

The problem of the rate of escape of gas from a supersaturated solution, and the factors which affect it, is one to which comparatively little attention has been given. Perman (T., 1895, **67**, 868; 1898, **73**, 511), by aspirating air through an aqueous solution of ammonia; Bohr (*Ann. Phys. Chem.*, 1899, [iii], **68**, 500), by passing air over the surface of an agitated aqueous solution of carbon dioxide; and Steele (T., 1903, **83**, 1470), by bubbling hydrogen through a solution of hydrogen chloride in toluene, found that the velocity with which the solutions were desaturated followed a logarithmic law; or the rate of desaturation was proportional to the concentration of the gas in the solution. By Carlson (*J. Chim. phys.*, 1911, **9**, 235) it has been found, more recently, that the logarithmic law is valid also for the rate of solution of oxygen and of carbon dioxide in water; and Bohr (*loc. cit.*) has shown that the ratio of the volume of gas which passes into solution through unit area in unit time (coefficient of invasion) to the volume of gas which similarly passes out of solution (coefficient of evasion) is constant, and equal to the absorption-coefficient.

It will be observed that the method of investigation employed hitherto is that of passing an indifferent gas through or over the solution, and the results obtained can, as has been pointed out by Meyer (*Zeitsch. Elektrochem.*, 1909, **15**, 249) and Carlson (*loc. cit.*), be interpreted in the light of the Nernst diffusion theory, which

has proved so useful in connexion with heterogeneous solid-liquid systems (compare, however, Roselli, *J. Chim. phys.*, 1911, **9**, 689).

The method adopted by us, however, is essentially different, and is more in accordance with the conditions actually encountered. Moreover, the systems which we have investigated are, on account of the presence of colloids, very different from the simple aqueous solutions of a gas hitherto studied. Whether the method of aspirating an indifferent gas through such solutions would yield results of the same character as those which have been obtained by the method described later, will be investigated in the immediate future.

#### *Apparatus and Method of Working.*

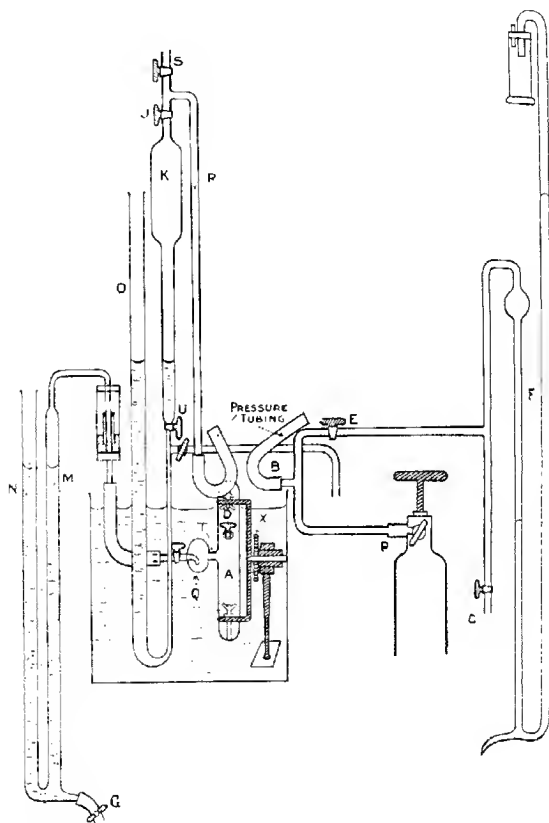
The apparatus employed, the outcome of the experience gained from a very large number of measurements, is represented diagrammatically in Fig. 1. The liquid from which the escape of gas is to be measured is contained in the solution-tube *A*, which is cylindrical in form, and is 25 cm. long and 3 cm. in diameter. To the ends of the tube are sealed two glass "trees," the purpose of which will be apparent later. Since it is necessary to employ in each experiment the same volume of solution, the tube *A* was calibrated, the volume being determined up to the mark *T* on the side-tube *Q*. This side-tube, which passes into the solution-tube at a point equidistant from the two ends, is connected by means of thick-walled rubber tubing and a mercury seal with a gas-measuring burette *M*. To prevent solution being carried by the escaping gas from the solution-tube to the mercury seal, a bulb trap and safety tube were blown on the side-tube *Q*. (The end of the safety tube was not as shown in the diagram, but was bent into the form of a loop.) About 10 ccm. from one end of the solution-tube there is another side-tube *D*, furnished with a well-fitting capillary glass tap. The solution-tube, *A*, is held by rubber bands in a suitable frame, to which a spindle, carrying a cog-wheel, *X*, is attached. This spindle passed through a ball-bearing held firmly in a clamp, the whole being immersed, as indicated in the figure, in the water of a thermostat. The mercury seal and the burettes *K* and *M*, which were outside the thermostat, were water-jacketed.

The solution-tube, having been fixed in the frame so that the side-tube *Q* was co-linear with the spindle of the frame, could be caused to revolve by means of an electric motor and a driving chain<sup>\*</sup> passing round the cog-wheel *X*. As the tube revolves, the

\* It may be mentioned that it was found to be quite essential to employ a chain drive. By connecting the cogged driving wheel, the axle of which ran in ball-bearings, with the low gear of the motor by means of a stretched rubber band, it was found that instantaneous starting of the solution tube could be effected.

rubber tubing attached to *Q* turns freely in a wide collar (not shown in the figure), and communicates the rotary movement along

FIG. 1.



its whole length. It thus acts as a universal joint.\* No difficulty

\* Although not absolutely necessary, owing to the rapidity with which the gas was evolved from the solutions, the precaution was adopted of coating the inside of the rubber tubing with a mixture composed of glycerol, glue, and water in the proportions 10 : 20 : 100, to prevent any diffusion of carbon dioxide through the rubber (*Gammeli Z. d. L.*, 1912, **26**, 1626).

was found in obtaining satisfactory results with this joint, provided such care is taken in making the mercury seal as to ensure smooth running. We have found, also, that there is no detectable difference in the volume-reading in the burette *M* when the solution-tube is rotated or is at rest. Should any change occur, therefore, in the bore of the pressure tubing which constitutes the universal joint, owing to torsion, such change is too small to alter sensibly the volume of gas measured.

By the revolution of the solution-tube, *A*, also, the solution is caused to pass from end to end of the tube, and in so doing it falls on the glass "trees," and is thereby broken up. In this way a very efficient agitation of the solution is effected.

In carrying out an experiment, one proceeds as follows: The solution-tube, having been carefully cleaned and washed out with a quantity of the colloidal or other solution to be investigated, is finally filled with the latter to rather above the graduation mark. During the washing process care is taken to avoid the entrance of air into the apparatus by forcing the liquids out of the tube by means of carbon dioxide. When the tube and its contents have acquired the appropriate temperature, the volume of the solution is adjusted to the graduation mark, and a definite volume is then forced out of the solution-tube by means of carbon dioxide, the volume of liquid retained in the tube being, in all cases, 30.00 c.c.

The solution-tube having been placed in position in the thermostat, the liquid is saturated with carbon dioxide under a definite pressure (about 760 mm. above the prevailing atmospheric pressure) by connecting the side-tube *D* with the cylinder *P* containing the compressed gas. By means of the tap *E*, connexion is also established with a manometer *F*, whereby the gas pressure can be determined. Saturation of the solution with gas having been effected with agitation, the solution-tube is fixed upright in an automatically removable clamp, and allowed to remain undisturbed for some time. This period of repose is of great importance in order to ensure a period of quiescence on reducing the pressure. While the solution-tube is in the upright position, the portion projecting above the water of the thermostat is bathed in a stream of thermostat water which is kept in circulation by means of a Luther pump.

After thirty minutes the solution-tube is connected through the side-tube *D* and the tube *R* with the "reduction burette," *K*. This "reduction burette," which, together with the connecting tube *R* and the reservoir tube *O*, is enclosed in a water-jacket, contains, as measuring liquid, a solution of sodium hydrogen carbonate saturated with carbon dioxide. This solution is drawn up so as to fill the burette up to the tap *J*, which is then closed. The pressure in

the tube *R* having been reduced to that of the atmosphere by opening and then closing the tap *S*, the taps *J* and *D* are opened, and communication thereby established between the solution-tube and the reduction burette. The gas in the solution-tube expands into the reduction burette, the negative pressure which obtains in the latter assisting the process. When the pressure in the reduction burette becomes equal to the atmospheric, the tap *D* is closed.\* By opening the tap on the side-tube *Q*, any further gas was collected in the water-jacketed "measuring burette," *M*. This volume, together with that of the gas collected in the reduction burette, constitutes the "reduction volume,"  $V_R$ .

In most cases it was found that escape of gas on reduction of the pressure to atmospheric was succeeded quite sharply by a period of quiescence during which no gas was evolved from the supersaturated solution. This period of quiescence, however, was obtained only when the solution was allowed to remain undisturbed for some time after saturation; for a period sufficiently long, in any case, to allow any froth, formed during saturation, to disappear. In certain cases, as will be described later, no quiescent period was obtained, and in the case of water the occurrence of a period of quiescence was somewhat irregular.

When the quiescent period set in, the burette reading was recorded, the solution-tube was unclamped and caused to revolve by starting the motor, and the rate of evolution of the gas from the supersaturated solution determined. As the gas passed over into the measuring burette, liquid was allowed to run out through the tube *G*, furnished with a spring clip, so that the pressure in the burette was always maintained equal to that of the atmosphere.

As the rate of escape of gas from the supersaturated solution was very great, it was found possible to measure it only by mechanical records on a rotating drum covered with smoked paper.† This drum was furnished with three writing points, actuated electromagnetically. One of these was connected with a clock beating half seconds, and so yielded a time line; a second point recorded the revolutions of the solution tube; whilst the third point was connected with a

\* The expulsion of the measuring liquid from the reduction burette was so rapid that there was no time for the liquid to drain from the walls. Accordingly, when atmospheric pressure had been established, the tap *U* was closed, and the volume reading taken after half an hour.

† Some idea of the velocity of evolution will be obtained when it is mentioned that in the case of concentrated gelatin solutions, 99.5 per cent. of the gas was evolved in 14.9 seconds, and during that time it was possible to obtain seventeen time-volume readings. It may also be stated that even with such rapid evolution of gas, volume readings could be made to 0.05 c.c.

tapping key, by means of which a signal could be sent at certain definite volume-readings on the measuring burette.

*Evolution of Carbon Dioxide from Unagitated Solutions.*

At the outset of this investigation a number of observations were made of the rate of escape of gas from unagitated supersaturated solutions. It has already been mentioned that on reducing the pressure of the gas above the solution to that of the atmosphere, a period of quiescence ensues, during which no gas escapes from the supersaturated solution. In this condition of metastability, however, the solution is exceedingly sensitive, a very slight mechanical shock being sufficient to cause a considerable evolution of gas. The occurrence of this period of quiescence is also prevented by even small traces of grease or dirt on the walls of the vessel, as well as by the presence of small particles of solid in the solution. Scrupulous care was therefore taken in the cleaning of the solution-tube.

The period of quiescence, however, did not persist indefinitely. After a shorter or longer time—in the case of certain gelatin solutions a period of twenty minutes was observed—a rather rapid spontaneous evolution of gas set in, which gradually diminished as the solution became desaturated. The diminution in the rate of escape of gas was, however, not continuous, but periodic, that is to say, the first rapid evolution gradually diminished to a certain extent when another comparatively rapid escape of gas took place. This was followed by an almost quiescent period, and at a certain point another comparatively rapid evolution of gas took place, and so on. This phenomenon, which does not seem to have been observed before, might perhaps be referred to changes in the surface layer of the liquid, but is probably to be explained more correctly as follows: Gas solutions, as has been known for long, readily remain supersaturated; that is to say, gaseous "nuclei" are formed with great difficulty. When, however, such nuclei are formed either in the body of the liquid or at the walls of the containing vessel, they will grow owing to diffusion into them of gas from the surrounding supersaturated solution. The bubbles attached to the walls of the vessel will, when they have acquired a certain size, detach themselves from the walls and escape. When these have escaped, nuclei again begin to be formed in the solution and on the walls of the vessel, and in the latter case they will, no doubt, be formed preferentially at the points where the bubbles were previously produced. These bubbles will increase in size as before, only more slowly as the solution becomes less concentrated, and the escape of this second series of bubbles, which, we may expect, will



grow at about the same rate, and therefore detach themselves from the walls of the vessel at about the same time, will give rise to a second period of relatively rapid evolution, and so on. One would therefore expect that as the solution becomes less concentrated and the process of diffusion becomes slower, the length of the periods between the points at which the relatively rapid evolution of gas occurs would become longer. This is found, indeed, in some measure to be the case, but not completely so; and the reason for this may be that the diminution in the rate of growth of the bubbles which act as nuclei is more than counterbalanced by the formation of a larger number of nuclei.

Although the period of quiescence is well marked in the case of water, solutions of dextrin, and, more especially, solutions of gelatin, it is wanting in the case of solutions of peptone and ferric hydroxide. In these cases gas is evolved immediately when the pressure over the solution is reduced to that of the atmosphere. Although in the case of peptone solutions spontaneous evolution of gas sets in immediately, the rate of this spontaneous evolution is sufficiently slow to be measurable; but in the case of solutions of ferric hydroxide the rate of evolution is immeasurably rapid. After this first period of rapid evolution, however, the process goes on as in the case of the other solutions. It would therefore appear that in the case of solutions of ferric hydroxide there exists no essential difference as compared with other colloids, but that the metastable region with regard to gaseous supersaturation is much less. It may be that if the other solutions were supersaturated to a higher degree (by saturating with carbon dioxide at a higher pressure), there would also be no period of quiescence on reducing the pressure. We have not, however, investigated this.

The following figures will give an indication of the rate of evolution of carbon dioxide from unagitated water solutions:

Time in minutes .....	1	3	7	14	24
Volume in c.c. ....	0.5	1	1.5	2	2.5

The rate of evolution differed in the case of different solutions, but in most cases, after a period of about thirty minutes, it assumed an average value of about 1 c.c. in fourteen minutes, the time-volume curves then becoming parallel.

Although a number of experiments were carried out with unagitated solutions their study was abandoned, at least for the present, because quantitatively reproducible results could not be obtained.

*Evolution of Carbon Dioxide from Agitated Supersaturated Solutions.*

As it was already well known from the work of others (Blanchard, *Zeitsch. physikal. Chem.*, 1902, **41**, 681; Walton, *ibid.*, 1904, **47**, 189; Lamplough, *Proc. Camb. Phil. Soc.*, 1908, **14**, 591) that gas supersaturation readily occurs in solution, and our own experiments having shown that no results of a sufficiently satisfactory or definite nature could be obtained with unagitated solutions, the apparatus previously described was devised to allow of the measurement of the evolution of gas from agitated solutions. With this apparatus a very large number of experiments have been carried out, and it has been found that results reproducible within narrow limits can be obtained.

For the purpose of obtaining an insight into the effect of various solutes or pseudo-solutes on the rate of evolution of gas, it is not sufficient merely to determine the volumes of gas evolved at given intervals of time, because of the fact that the total amount of gas evolved from equal volumes of solution has different values. The time-volume curves, therefore, although indicating differences in the case of different colloids, are not sufficiently distinctive, and cannot be compared directly with one another (see Fig. 2).

It has already been pointed out that Meyer (*loc. cit.*) has shown (on the basis of experiments by W. F. Knox) that the rate of removal of carbon dioxide from solution by a stream of air is proportional to the concentration of the carbon dioxide in the solution. If, in the cases studied by us, it is assumed that the rate of evolution is proportional to the degree of supersaturation, we obtain as the expression for the velocity of evolution,  $\frac{dv}{dt} = k\left(1 - \frac{v}{V}\right)$ , where  $v$  is the volume of gas evolved at time  $t$  (in seconds) and  $V$  the total volume evolved. The term  $\left(1 - \frac{v}{V}\right)$ , therefore, represents the degree of supersaturation. On integration, this equation yields

$$k = \frac{2.30}{t} \cdot \log_{10}\left(1 - \frac{v}{V}\right).$$

Here  $k$  has a negative value, since the term  $\left(1 - \frac{v}{V}\right)$  is less than unity. Justification for the adoption of this equation as a basis on which comparison of the behaviour of different solutions can be instituted was found in the fact that in the case of the escape of gas from supersaturated solutions of carbon dioxide in pure water, the value of the coefficient  $k$  is nearly constant. Moreover, the slight deviation from constancy which is found is proportional to

the degree of supersaturation, so that when one plots the values of  $k$  against the degree of supersaturation a straight line is obtained. By plotting the values of the velocity-coefficient against the degree of supersaturation in the case of different solutions, we have a means of representing clearly the distinctive and characteristic behaviour of colloids as affecting the escape of gas from supersaturated solution.

#### *Method of Calculation.*

As is obvious, the expression given above is that of a unimolecular reaction; and if the rate of escape of gas from supersaturated solutions were strictly unimolecular, it would not matter from what stage of the evolution process the volume of gas were calculated. As a matter of fact, however, it is found that in the case of colloidal solutions the escape of gas is by no means a true unimolecular reaction; and even in the case of pure aqueous solutions a slight but definite trend in the value of  $k$  is observable. It is necessary, therefore, to employ in the calculation of the velocity-coefficient values of  $t_0$  and  $v_0$  which shall be strictly comparable in the different cases. Unfortunately, it is not possible to employ the natural zero of time, namely, the moment at which evolution from the solution commences, on account of the time required (two to three seconds) to set up uniform agitation. This indefiniteness in the zero point is shown by the fact that none of the time-volume curves passes through the origin (Fig. 2). We have therefore selected as the zero time that point at which there remains in solution three-fourths of the theoretical amount of carbon dioxide in excess of that required to saturate the solution. This can be obtained from the solubility values determined by Findlay and Creighton and by Findlay and Shen. The value of  $v_0$  having been calculated in this way, the corresponding time value can be obtained from the time-volume curve.

To give an indication of the accuracy of the experimental results we have given, at the head of each table, the total volume of gas evolved as actually measured ( $V_e$ ) and as calculated from the solubility value ( $V_t$ ), due regard being paid to the pressure of saturation and the pressure at which the gas was evolved. These pressures are represented by  $B_s$ , the barometric pressure at the time of saturation with gas;  $B_e$ , the barometric pressure at the time of evolution of gas; and  $M$ , the manometric pressure. ( $M + B_s$ ), therefore, represents the total pressure under which saturation with gas was carried out.

An example will render the method of calculation clearer. In the case of water (table I), for example, the solubility of carbon dioxide is 0.817. Since the volume of water in the solution-tube

is 30.0 c.c. (p. 1173), we can imagine that the water is removed, and that we are dealing with carbon dioxide contained in an actual volume of  $30.0 \times 0.817 = 24.51$  c.c. When saturation of the solution takes place, we can imagine that carbon dioxide is compressed into the volume of 24.51 c.c. under a pressure of  $(M + B_s) = 1493.1$  mm. On reducing the pressure to  $B_s = 745.0$  mm., and allowing carbon dioxide to escape, the volume which escapes should be, theoretically:

$$V_t = \frac{24.51 \times 1493.1}{745.0} - 24.51 = 24.60.$$

To obtain the zero volume on the "three-fourths basis" referred to above, we have  $v_0 = (V_s - \frac{3}{4}V_t)$ . Hence, again taking the data from

FIG. 2.

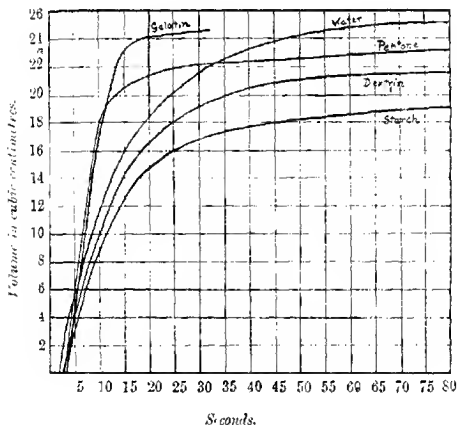


table I, we obtain  $v_0 = 24.55 - 18.46 = 6.09$ . From the time-volume curve, one obtains the corresponding time value  $t_0 = 7.5$ . The corrected values of time and volume are then obtained by subtracting 7.5 secs. from the direct time readings, and 6.09 c.c. from the corresponding volume readings.

The correctness of the observed volume of gas evolved can be checked, not only by comparing the values of  $V_s$  and  $V_t$  (which can be done when the quiescent period is well marked), but also by measuring the "reduction volume"  $V_r$ . If the gas space in the solution tube is represented by  $V_0$ , the correct "reduction volume," or the volume of gas which should escape from the

solution-tube, owing to the expansion of the compressed gas, should be:

$$V_{ec} = \frac{V_e \times M + B_s}{B_e} - V_e = V_e \frac{M + B_s - B_e}{B_e}.$$

By comparing the value of  $(V_e + V_R)$  with  $(V_t + V_{ec})$ , the correctness of the total volume reading can be checked. Thus, from the data in table I, we have  $(V_e + V_R) = (24.55 + 127.9) = 152.45$ ; and  $(V_t + V_{ec}) = (24.6 + 128.2) = 152.8$ . This check is especially useful when there is no distinct quiescent period. In those cases where the solubility varies with the pressure, due regard must be paid to the fact in making the calculations.

#### EXPERIMENTAL.

In all the experiments recorded here the temperature employed was 25.0°. The carbon dioxide was taken from a cylinder of commercial gas, which contained 0.33 per cent. of impurity, a fact which must be borne in mind when one employs the solubility data for the gas. It ought also to be stated that it is of essential importance to work with air-free solutions, and to expel all air from all the tubes of the apparatus. Another factor of the utmost importance is time. In the case more especially of gelatin and starch solutions, the time taken in the preparation of the solutions, the period during which the solutions remained in contact with the carbon dioxide, etc., were found to exercise a marked effect on the slope of the curve obtained. The whole series of operations in connexion with the different solutions were therefore carried out according to a very strict time table. When this was done, and all other conditions kept constant, velocity-supersaturation curves exactly reproducible as regards their slope could be obtained, although the absolute values of the velocity-coefficients might vary slightly.

With regard to the rotation of the solution-tube, the speed of 20 revolutions per minute was chosen as giving a velocity of evolution of gas which is measurable and reproducible. The influence of the speed of rotation is, however, not very great, and the variations which occurred in the course of the work are negligible in this respect. The speed of rotation is given at the head of each table, and is represented by  $R$ .

#### 1. Water.

A very large number of experiments (more than 120) have been carried out with solutions of carbon dioxide in water; and the following results may be taken as typical of all. In this table we

have also given the corrected times and volumes, that is, the times and volumes as measured from the value of  $t_0$  and  $v_0$ .

TABLE I.

$M=748.2$ mm.		$V_c=24.55$	$V_R=127.9$	$t_0=7.5$	
$B_1=744.9$		$V_i=24.60$	$V_{RG}=128.2$	$v_0=5.99$	
$B_2=745.0$		Solubility=0.817 $R=18.7$			
Time.	Volume.	Corrected time.	Corrected volume.	Super-saturation.	-k.
5.1	3.1	—	—	—	—
6.7	5.1	—	—	—	—
8.55	7.1	0.85	1.01	0.945	0.0606
10.15	9.1	2.65	3.01	0.837	0.0672
13.35	12.1	5.85	6.01	0.674	0.0673
14.65	13.1	7.15	7.01	0.620	0.0668
17.80	15.1	10.3	9.01	0.512	0.0650
21.55	17.1	14.05	11.01	0.404	0.0646
26.65	19.1	18.15	13.01	0.295	0.0637
34.20	21.1	26.7	15.01	0.185	0.0632
55.80	23.6	48.3	17.51	0.051	0.0614
$\infty$	24.55	$\infty$	18.46	—	—

## 2. Solutions of Potassium Chloride.

The velocity of evolution of carbon dioxide from solutions of potassium chloride of various concentrations has been investigated, and the following table reproduces the results obtained with the most concentrated solution.

TABLE II.

Concentration: 60.00 grams of potassium chloride in 1 litre of solution.

$M=761.0$ mm.		$V_c=22.60$	$V_R=127.7$	$t_0=7.35$
$B_1=759.0$		$V_i=22.58$	$V_{RG}=127.9$	$v_0=5.66$
$B_2=759.0$		Solubility=0.765		$R=29.3$
Time.	Volume.	Supersaturation.	-k.	
3.9	2.8	—	—	
5.1	3.8	—	—	
7.4	5.8	—	—	
10.0	8.8	0.918	0.0615	
13.8	10.8	0.815	0.0576	
15.3	10.8	0.697	0.0561	
21.3	11.8	0.637	0.0566	
31.6	14.8	0.461	0.0555	
43.6	17.8	0.285	0.0518	
53.1	19.8	0.167	0.0494	
	20.8	0.107	0.0487	

*Colloidal Solutions.*—The rate of evolution of carbon dioxide from solutions containing colloids was also determined. Before use, the solutions were filtered through a Hirsch funnel in order to eliminate the effect of solid particles on the velocity of evolution (Veley *Phil. Trans.*, 1888, A, 179, 264).

Vol. CIII

## 3. Solutions of Gelatin.

For these experiments Coignet's Gold Medal French gelatin was used. It was found to be very free from insoluble matter.

TABLE III (compare Fig. 3).

Concentration: 0.242 gram of gelatin in 1 litre of solution.

$M=760.2$ mm.	$V_c=25.5$	$V_R=130.0$	$t_0=7.75$
$R_1=742.5$	$V_s=25.13$	$V_{Rc}=130.9$	$v_0=6.65$
$R_2=742.1$	Solubility=0.817		$R=20$
Time.	Volume.	Supersaturation.	$-k$ .
3.5	1.6	—	—
5.4	3.6	—	—
6.1	4.6	—	—
7.7	6.6	—	—
11.6	11.6	0.738	0.0791
13.3	13.6	0.631	0.0629
15.3	15.6	0.525	0.0852
16.3	16.6	0.472	0.0877
17.4	17.6	0.419	0.0901
18.7	18.6	0.366	0.0917
20.0	19.6	0.313	0.0948
23.6	21.6	0.207	0.0934
26.0	22.6	0.154	0.1025

TABLE IV (compare Fig. 3).

Concentration: 0.231 gram of gelatin in 1 litre of solution.

$M=755.3$ mm.	$V_c=25.6$	$V_R=128.5$	$t_0=7.35$
$R_1=746.9$	$V_s=24.78$	$V_{Rc}=128.6$	$v_0=6.41$
$R_2=747.1$	Solubility=0.817		$R=20.5$
Time.	Volume.	Supersaturation.	$k$ .
2.95	1.0	—	—
5.1	3.0	—	—
5.8	4.0	—	—
7.1	6.0	—	—
8.9	8.8	0.872	0.0891
10.25	11.0	0.753	0.0977
11.4	13.0	0.646	0.1079
13.5	16.0	0.484	0.1178
15.1	18.0	0.377	0.1258
16.0	19.0	0.322	0.1309
19.85	22.0	0.161	0.1459
22.1	23.0	0.108	0.1510
26.2	24.0	0.054	0.1549

TABLE V (compare Fig. 3).

Concentration: 0.502 gram of gelatin in 1 litre of solution.

$M = 759.5$ mm.	$V_s = 24.25$	$V_R = 129.1$	$t_s = 6.55$
$B_s = 7.176$	$V_R = 24.90$	$V_{sc} = 129.7$	$r_0 = 5.57$
$B_r = 7.476$	Solubility = 0.817		$H = 19.3$

Time.	Volume.	Supersaturation.	$k$
4.7	2.5	—	—
6.0	4.5	—	—
6.5	5.5	—	—
8.1	8.5	0.843	0.1069
9.1	10.5	0.736	0.1199
10.1	12.5	0.629	0.1365
10.7	13.5	0.576	0.1328
11.8	15.5	0.469	0.1443
13.8	18.5	0.398	0.1625
15.7	20.5	0.291	0.1752
19.0	22.5	0.094	0.1909
23.5	23.5	0.049	0.1896

FIG. 3.

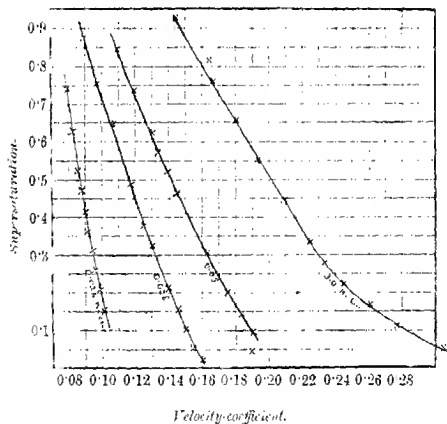




TABLE VI (compare Fig. 3).

Concentration: 30.01 grams of gelatin in 1 litre of solution.

$M = 759.2$ mm.	$V_s = 24.4$	$V_R = 128.8$	$t_0 = 5.7$
$B_s = 755.1$	$V_T = 24.51$	$V_{RC} = 128.6$	$v_0 = 6.02$
$B_s = 755.0$	Solubility = 0.825 and 0.819 at $B_s$ and at $(M + B_s)$ respectively		
$R = 22$			
Time.	Volume.	Supersaturation.	$-k$ .
4.0	2.3	—	—
5.0	4.3	—	—
5.1	5.3	—	—
6.2	7.3	0.930	0.1440
6.9	9.3	0.822	0.1680
7.3	10.3	0.767	0.1656
8.4	12.3	0.658	0.1816
9.6	16.3	0.441	0.2098
10.6	18.3	0.332	0.2249
11.8	20.3	0.223	0.2454
12.5	21.3	0.170	0.2615
13.5	22.3	0.115	0.2771
14.9	23.3	0.060	0.3066
19.0	24.3	0.006	0.3364

## 4. Solutions of Dextrin.

Kahlbaum's pure dextrin was employed, and a large number of readings were recorded with varying concentrations. The following are selected as representative.

TABLE VII.

Concentration: 10.0 grams of dextrin in 1 litre of solution.

$M = 756.6$ mm.	$V_s = 23.9$	$V_R = 125.9$	$t_0 = 9.7$
$B_s = 767.5$	$V_T = 24.19$	$V_{RC} = 125.6$	$v_0 = 5.55$
$B_s = 767.3$	Solubility = 0.812		
$R = 22$			
Time.	Volume.	Supersaturation.	$-k$ .
4.6	3.0	—	—
6.2	5.0	—	—
7.0	6.0	—	—
8.8	8.0	0.867	0.0687
10.8	10.0	0.757	0.0679
11.7	11.0	0.702	0.0767
14.2	13.0	0.594	0.0694
17.2	15.0	0.485	0.0689
21.4	17.0	0.376	0.0665
27.0	19.0	0.267	0.0593
76.3	23.5	0.022	0.0511

TABLE VIII.

Concentration: 30.0 grams of dextrin in 1 litre of solution.

$M = 763.4$ mm.	$V_s = 24.55$	$V_R = 130.4$	$t_0 = 7.9$
$P_s = 744.8$	$V_f = 24.95$	$V_{fc} = 131.1$	$v_0 = 5.84$
$P_f = 741.0$	Solubility = 0.804 and 0.801 at the pressures of saturation and evolution		
$R = 21.1$			
Time.	Volume.	Supersaturation.	-k.
5.1	3.5	—	—
5.8	4.5	—	—
9.3	8.5	0.858	0.0666
12.4	11.5	0.697	0.0667
13.5	12.5	0.614	0.0676
18.9	14.5	0.537	0.0627
21.6	16.5	0.430	0.0577
28.2	18.5	0.323	0.0533
33.3	19.5	0.270	0.0498
39.0	20.5	0.216	0.0466
44.8	21.0	0.190	0.0439

TABLE IX.

Concentration: 125.1 grams of dextrin in 1 litre of solution.

$M = 759.6$ mm.	$V_s = 23.2$	$V_R = 130.1$	$t_0 = 6.55$
$P_s = 741.1$	$V_f = 23.37$	$V_{fc} = 130.9$	$v_0 = 5.67$
$P_f = 741.1$	Solubility = 0.753 and 0.746 at saturation and at evolution pressures respectively		
$R = 21.0$			
Time.	Volume.	Supersaturation.	-k.
4.1	2.0	—	—
5.6	4.0	—	—
6.1	5.0	—	—
7.8	7.0	0.924	0.0826
9.3	9.0	0.810	0.0828
13.1	13.0	0.582	0.0821
15.0	14.0	0.525	0.0789
19.0	16.0	0.411	0.0732
25.3	18.0	0.297	0.0658
30.2	19.0	0.240	0.0612
49.1	20.5	0.154	0.0557
61.7	22.0	0.069	0.0483
118.0	23.0	0.011	0.0402

## 5. Solutions of Starch.

Kallbaum's soluble starch was employed. As it was found that the form of the curve for the velocity-coefficient against supersaturation depends on the history of the solution, the results of only one series of measurements are communicated, a fuller investigation of the behaviour of starch solutions being reserved for a future time.

TABLE X (compare Fig. 4).

Concentration: 30.0 grams of starch in 1 litre of solution.

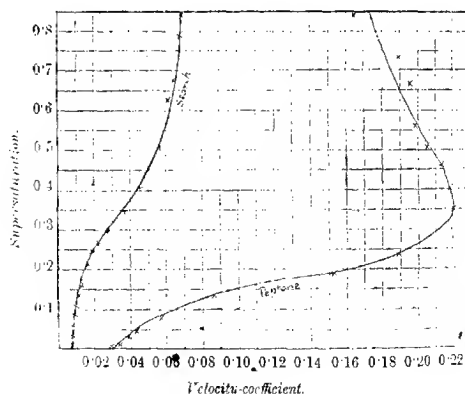
$M = 753.0$ mm.	$V_s = 23.75$	$V_R = 128.3$	$t_0 = 7.0$
$B_s = 747.7$	$V_t = 24.79$	$V_{RC} = 128.7$	$v_3 = 5.2$
$B_r = 747.5$	Solubility = 0.806 and 0.700 at saturation and		
$R = 21$	at evolution pressures respectively		
Time.	Volume.	Supersaturation.	$-k$ .
3.2	1.2	—	—
5.3	3.2	—	—
6.1	4.2	—	—
7.9	6.2	—	—
9.6	8.2	0.887	0.0686
10.6	9.2	0.783	0.0680
13.1	11.2	0.675	0.0643
16.5	13.2	0.568	0.0596
22.0	15.2	0.460	0.0517
35.8	17.2	0.352	0.0362
82.0	19.2	0.245	0.0188
132.0	20.3	0.186	0.0134
252.0	21.8	0.105	0.0093
392.0	22.6	0.062	0.0072
587.0	23.4	0.019	0.0068

## 6. Solutions of Peptone.

In these experiments commercial peptone (Witte's peptone) was used. It consists largely of albumoses (Mann, *Chemistry of Proteids*, p. 179), and contains a considerable quantity of insoluble material.

Since the form of curve is very different from that obtained with

FIG. 4.



other solutions, we propose to study these solutions more fully at a later date. Solutions of only one concentration of peptone have been investigated, but the form of the curve has been confirmed by three distinct experiments. As has already been mentioned, solutions of peptone exhibit no well-defined quiescent period, and they are further distinguished from the solutions previously described by the fact that there is a much greater production of froth.

As the value of the solubility of carbon dioxide given by Findlay and Shen refers to pure carbon dioxide, we have used a proportionately lower value for the commercial carbon dioxide employed by us.

TABLE XI (compare Fig. 4).

Concentration: 7.58 grams of peptone in 1 litre of solution.

$H_0 = 753.9$ mm.	$V_0 = 23.5$	$V_H = 127.5$	$t_0 = 1.05$
$H_1 = 760.9$	$V_1 = 24.43$	$V_{H0} = 124.9$	$t_m = 5.2$
$H_2 = 769.5$	Solubility = 0.838 and 0.855	$H = 29$	
Time.	Volume.	Supersaturation.	$-k$ .
3.3	3.1	—	—
4.0	5.1	—	—
4.35	6.1	—	—
5.1	8.1	0.842	0.164
5.7	10.1	0.732	0.189
6.1	11.1	0.671	0.195
6.9	13.1	0.568	0.195
7.3	14.1	0.514	0.205
7.7	15.1	0.459	0.213
8.8	17.1	0.356	0.221
11.6	19.1	0.211	0.189
27.7	21.1	0.131	0.086
74.0	22.6	0.049	0.043
153.0	23.3	0.011	0.028

### 7. Solutions of Ferric Hydroxide.

As has already been mentioned, solutions of ferric hydroxide supersaturated with carbon dioxide show no quiescent period on reducing the pressure. After a period of rapid evolution, however, the solutions become quiet although still supersaturated to some extent. These solutions were then shaken, and the velocity-coefficient of gas evolution was determined, zero time being taken as the moment when agitation was commenced. As we are here dealing with solutions from which a great portion of the dissolved gas has already escaped, the values of the velocity-coefficient are not strictly comparable with those obtained in the previous cases. In the following tables we have calculated the velocity-coefficient on the basis of the total volume of gas evolved after the first rush of gas had ceased and quiescence had set in.

TABLE XII.

Concentration : 13.53 grams of ferric hydroxide in 1 litre of solution.

$M=758$ mm.	$B=762$	$V_s=9.5$	$R=20.3$
Time.	Volume.	Supersaturation.	$-k$ .
3.5	2.0	0.790	0.067
5.3	3.0	0.685	0.072
8.6	4.5	0.527	0.074
12.5	5.5	0.452	0.069
15.1	6.0	0.369	0.066
20.6	7.0	0.264	0.064
31.8	8.0	0.158	0.058

TABLE XIII.

Concentration : 3.767 grams of ferric hydroxide in 1 litre of solution.

$M=763.2$ mm.	$B=755.5$	$V_s=14.6$	$R=20$
Time.	Volume.	Supersaturation.	$-k$ .
5.6	3.4	0.767	0.047
6.1	3.9	0.733	0.048
7.6	4.9	0.665	0.054
9.1	5.9	0.596	0.057
9.8	6.4	0.561	0.063
13.2	8.4	0.425	0.065
15.5	9.4	0.356	0.067
19.7	10.9	0.256	0.069
23.4	11.9	0.187	0.072
29.4	12.9	0.117	0.073

## 8. Colloidal Solutions of Platinum.

The escape of carbon dioxide from colloidal solutions of platinum, prepared by Bredig's method, showed practically no difference as compared with the escape from pure water.

## 9. Solutions of Agar.

For the purpose of comparison with solutions of gelatin, one experiment was carried out with a solution of agar, the concentration of the latter being 1.522 grams in 1 litre of solution. As the solubility of carbon dioxide in solutions of agar is not recorded, the values of  $k$  were calculated solely from the volumes of gas evolved, measured from the moment when shaking commenced. In the following table we give, for the sake of shortness, only the values of supersaturation and the calculated value of the coefficient.

TABLE XIV.

Supersaturation .....	0.76	0.66	0.46	0.27	0.12	0.051
$-k$ .....	0.033	0.039	0.059	0.054	0.055	0.072

10. *Suspensions of Charcoal.*

A fine suspension of Kahlbaum's bone charcoal was employed. When the saturation with carbon dioxide was carried out, as in the previous experiments, by allowing the carbon dioxide to remain in contact with the suspension for an hour and a-half, a curve resembling that for pure water was obtained. If, however, the saturation was prolonged over a period of forty-eight hours, the results given in the following table were obtained. Since, in this experiment, the total volume of gas evolved did not equal that calculated from the solubility data of Findlay and Creighton, the values of  $k$  were calculated from the actual volumes measured. The zero of time was again calculated from the point at which the degree of supersaturation was 0.75 on the basis of the total volume of gas evolved.

TABLE XV.

Time.	Volume.	Supersaturation.	$-k$ .
13.8	9.4	0.80	0.032
15.5	10.4	0.75	0.042
19.5	12.1	0.63	0.042
25.4	14.1	0.52	0.039
29.0	15.4	0.46	0.039
36.9	16.9	0.38	0.031
63.9	18.9	0.27	0.024
102.0	19.9	0.21	0.017
155.1	20.5	0.18	0.012
252.9	21.5	0.12	0.009
367.0	22.3	0.07	0.007
827.0	23.3	0.02	0.005

*Discussion of Results.*

A consideration of the results communicated in the preceding pages will show that in the case of unagitated solutions, supersaturation can occur to a very marked extent, solutions of gelatin, especially, which had been saturated at a pressure of about two atmospheres, remaining quite quiescent and evolving no gas when the pressure was reduced to one atmosphere. As mentioned, however, this period of quiescence is one during which the solution is in a very sensitive metastable state, and this may perhaps account for the fact that in connexion with the velocity of certain reactions as studied by the amount of gas evolved, considerable discussion has been evoked with regard to the importance of shaking the solutions (Lamplough, *loc. cit.*; Veley, *Trans. Faraday Soc.*, 1909, 5, 1). Our experiments certainly show that with carefully cleaned apparatus and in the absence of mechanical shock, supersaturation can occur to a very marked extent.

With regard to the escape of gases from agitated solutions, our

experiments show that the rate of escape of carbon dioxide from pure supersaturated aqueous solutions, is very nearly proportional to the degree of supersaturation. In all cases, however, the value of the velocity-coefficient was found to diminish to a slight extent as the supersaturation diminished; and this diminution appears to be an essential, and not merely a chance phenomenon, as it was found even with different apparatus, and was in all cases practically the same in amount.

As long ago as 1869, it was observed by H. Müller (T., 1870, 23, 37), in connexion with the manufacture of soda-water, that "in order to make the water take up carbonic acid gas in such a manner that the gas may not be immediately disengaged when the liquid is let out of the apparatus, it is necessary that the gas and water be left together in the apparatus for at least twenty-four hours. If the agitation is continued merely for an hour or an hour and a-half, then, on letting out the water, the carbonic anhydride instantly disengages itself, the water becomes creamy, the gas comes up immediately, and the effervescence is over; whereas, if the gas be allowed to remain in contact with the water from twenty to twenty-four hours, and the liquid be then let out, the carbonic anhydride disengages itself from the water gradually, and attacks itself to the sides of the glass, seeming, indeed, to be altogether in a different state to that in which it is, after being left for only a short time in contact with the water. It appears, indeed, that in one case, that is, after a short contact, the carbonic anhydride dissolves in the water merely as such, but that after prolonged contact it becomes hydrated, and is dissolved by the water as hydrogen carbonate, or carbonic acid, and is then retained more firmly." We have not been able to obtain any confirmation of such a difference, no variation in the velocity of evolution of carbon dioxide having been observed, although the period of saturation with carbon dioxide under pressure varied from about an hour and a half up to three weeks. The explanation of the behaviour observed by Müller is most probably to be found in the presence of grease or other matter on the walls of the glass or of solid particles suspended in the liquid. These materials retain minute quantities of air, which then acts as a "nucleus," and brings about the evolution of the carbon dioxide from the supersaturated solution. When the process of saturation is continued for a lengthened period, the air retained by the solid particles will get dissolved, and there will consequently be no "nuclei" to initiate the evolution of the carbon dioxide. The very important effect of even traces of grease in overcoming supersaturation has been

observed by a number of investigators, as well as most distinctly by our ourselves. Most scrupulous care in cleaning the solution-tube had to be exercised, if a distinct quiescent period was to be obtained.

The phenomenon of the escape of gas from supersaturated aqueous solution is a comparatively simple one; and so also does it appear to be in the case of solutions of electrolytes, such as potassium chloride, which appear to have no influence, or practically none, on the rate of evolution of carbon dioxide from supersaturated solution. Quite otherwise is it, however, when colloids are present in solution. In this case the phenomenon becomes much more complicated, and considerable differences are found in the case of the different colloidal solutions.

Even the direct time-volume curves (Fig. 2) show that there is a marked difference in the behaviour of different colloids. Thus, in the case of solutions of gelatin, peptone, ferric hydroxide, and agar, there is a much more rapid evolution of gas initially than is found in the case of water, and solutions of potassium chloride, dextrin, or starch. The differences are, however, more obvious when one considers the velocity-coefficient-supersaturation curves and tables. From these one sees that dextrin has not a very marked influence on the rate of escape even when the concentration of the dextrin is 3 per cent. It is noticeable, however, that there is a marked diminution of the velocity-coefficient as the degree of supersaturation diminishes. This behaviour is not characteristic of dextrin, however, but it found also in the case of other colloids; starch shows it very conspicuously as well as the ferric hydroxide solution of 0.38 per cent. concentration. In the case of suspensions of charcoal, a similar very marked diminution of the velocity-coefficient is observed in those cases, and only in those cases where the suspension was kept in contact with the carbon dioxide for a lengthened period. We are led by this behaviour on the part of charcoal to think of the relatively slow rate of absorption of carbon dioxide by charcoal which follows on the period of comparatively rapid absorption (Findlay and Creighton, *loc. cit.*), and to explain the falling off in the value of the velocity-coefficient to a slow outward diffusion of the carbon dioxide dissolved in the charcoal. Whether this should prove to be a true explanation or not, it is noteworthy that in the case of starch also, Findlay and Creighton found that saturation with carbon dioxide takes place more slowly than in the case of other colloids studied by them.

A markedly different behaviour is found in the case of solutions of gelatin and of agar, the former having been most fully



investigated. In these cases the velocity-coefficient increases with diminution in the supersaturation, and the more so the greater the concentration of the gelatin.

Still more conspicuous in its behaviour is peptone. In this case, as, more pronouncedly, in the case of ferric hydroxide, there was no quiescent period on releasing the pressure of gas above the supersaturated solution. There is a comparatively rapid evolution of carbon dioxide until the supersaturation has diminished to about half, and then the velocity-coefficient rapidly falls away, owing to the very slow rate at which the gas is evolved. As the peptone used by us has been shown to consist largely of albumoses, its behaviour is of interest from the point of view of the manufacture and the palatability of aerated beverages, since beers contain appreciable amounts of albumoses. Their effect would therefore be to delay the occurrence of "flatness" in the beer.

There is, however, one property to which casual reference only has been made, but which exercises an important influence on the rate of escape of gas from solutions of gelatin and of starch; that is, the change which was found to take place in gelatin and starch solutions on being kept in contact with carbon dioxide for varying periods of time, or on being repeatedly re-saturated with carbon dioxide. In such cases, the characteristic influence of the gelatin and starch disappeared, and the behaviour approached to that with pure water. This question of ageing is one of great importance, and we hope to investigate and report on this matter more fully at a later time.

For the varied behaviour of the different colloids, no explanation can as yet be offered. One is, of course, inclined at first to try to bring the process of evolution into relation with the viscosity and surface tension of the solutions; and, certainly, one would be inclined to expect that these properties would exercise some influence on the behaviour of the solutions. The rapid evolution from peptone solutions, for example, might be referred to the diminished surface tension; but the difficulty would still remain, that the last third of the gas escapes with great slowness. The question, however, merits fuller investigation, and we hope to determine the viscosity and surface tension of the solutions we have used both before and after saturation with carbon dioxide. Meanwhile we offer the report on the experiments we have so far carried out as a first contribution to the study of a very complex problem.

The experimental work described in this paper was carried out in

the Chemistry Department of the University of Birmingham, and we are indebted to Prof. Frankland for the many facilities which he placed at our disposal.

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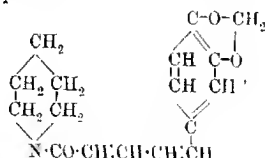
### XXIII.—*The Relation between the Absorption Spectra and Constitution of Piperine, Nicotine, Cocaine, Atropine, Hyoscyamine, and Hyoscyne.*

By JAMES JOHNSTON DOBBIE and JOHN JACOB FOX.

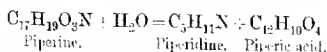
In recent papers (T., 1911, 99, 1254; 1912, 101, 77) it was shown that each of the alkaloids cinchonine, quinine, and cupreine gives an absorption spectrum which is almost identical with the spectrum of that part of the molecule of the alkaloid which is unreduced; piperidine in the case of cinchonine, 6-methoxy- and 6-hydroxypiperidine in the cases of quinine and cupreine respectively.

We have obtained similar results with other alkaloids of known constitution, in which a reduced is combined with an unreduced nucleus. The alkaloids examined in this connexion were piperine, nicotine, cocaine, and atropine, which, as will be seen from the foregoing, give spectra differing widely from one another.

The alkaloid piperine:



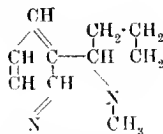
obtains piperidine in combination with the piperic acid residue, and, under the influence of hydrolytic agents, yields piperidine and piperic acid:



Piperidine is a completely reduced substance, and its alcoholic solution gives no absorption bands. Piperic acid, on the other hand, contains an unreduced benzene nucleus; its spectrum exhibits

strong absorption, and contains a wide absorption band the head of which lies at  $1/\lambda$  3070. On comparing the absorption curve of piperic acid with that of piperine, the two are seen to be almost identical.

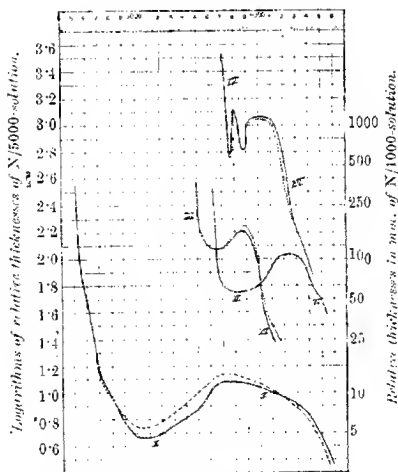
Nicotine has a pyridine ring united with a methylpyrrolidine which is completely reduced.



Nicotine.

The curve of the absorption spectrum of nicotine closely resembles that of the picolines (Baly and Baker, T., 1907, **91**, 1122; Purvis,

*Oscillation frequencies.*

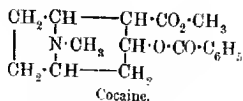


- I. Full curve: *Piperine*. Dotted curve: *Piperic acid*.  
 II. *Nicotine*.  
 III. Full curve: *Cocaine*. Dotted curve: *Benzoic acid*.  
 IV. Full curve: *Atropine*, *homocytanine* and *hyoscyne*. Dotted curve: *Tropaeol*.

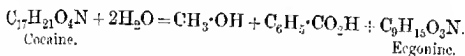
(ibid., 1909, **95**, 296). In this case the spectrum is similar to that of a simple homologue of pyridine, and the head of the band lies at about  $1/\lambda$  3840. This is almost midway between the heads of

the bands for  $\alpha$ - and  $\beta$ -picoline. From the point of view of absorption spectra nicotine may therefore be regarded as a homologue of pyridine.

In cocaine the molecule is much more complex than that of the two alkaloids already considered:

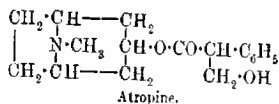


On boiling with concentrated mineral acids, cocaine breaks up into benzoic acid, methyl alcohol, and ecgonine:

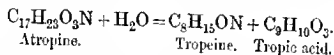


In this case the unreduced nucleus is a benzoic acid residue, and the spectrum of the alkaloid is identical with that of benzoic acid, as described by Hartley (T., 1907, 91, 319). The presence or absence of the band in the spectrum of benzoic acid has been the subject of some discussion, but we are able to confirm the existence of the shallow band recorded by Hartley and Hedley (*loc. cit.*).

The case of atropine is of special interest on account of the close connexion of this alkaloid with hyoscyamine and hyoscine:



As is well known, atropine is an optical isomere of hyoscyamine, and we find that the spectra of these two alkaloids are identical. When atropine is acted on by hydrolytic agents, it splits up into tropine and tropic acid:

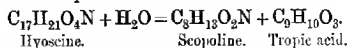


Similar products are given by hyoscyamine. Tropine is a fully reduced substance, whereas tropic acid contains an unreduced benzene nucleus.

The spectrum of tropic acid is peculiar. It contains two very narrow bands, having their heads at  $1/\lambda 3770$  and  $1/\lambda 3870$ ; this spectrum is the same as that of atropine and hyoscyamine.

Another point of great interest in connexion with the absorption spectra of this group of alkaloids is that, although hyoscine (*scopolamine*),  $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}$ , differs in composition from hyoscyamine,

it gives the same spectrum. The products of hydrolysis of hyoscyne are scopoline and tropic acid:



The constitution of scopoline has not been completely elucidated, but it is known to be a wholly reduced substituted pyridine. The unreduced portion is the same in all three alkaloids, namely, tropic acid; the differences occur entirely in the reduced portion of the molecule, and, as has been pointed out in the case of the cinchonine group of alkaloids (T., 1911, 99, 1261), such differences may exist without disturbance of the spectrum. The identity of the spectrum of hyoscyne with that of atropine and hyoscyamine is thus satisfactorily accounted for.\*

In all these cases, therefore, it would appear that the same relation exists as in the earlier cases examined, in which reduced and unreduced rings are conjoined. Whilst absorption appears to be an additive property when the members of the same homologous series are compared with one another, it is remarkable that it is possible to add large groups to such nuclei as quinoline, pyridine and benzoic acid with only very slight effect on their spectra.

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#### CXXIV.—*A Case of Isomerism in the Methylated Ferrocyanides.*

By ERNALD GEORGE JUSTINIAN HARTLEY.

IN a previous communication (T., 1910, 97, 1729) the author described the preparation of tetramethyl ferrocyanide from hexamethylferrocyanogen chloride,  $(\text{CH}_3)_6\text{FeC}_6\text{N}_6\text{Cl}_2$ , by heating the latter under diminished pressure, two molecular proportions of methyl chloride being given off. An analysis of the crude substance so obtained gave numbers which were in good agreement with the formula  $(\text{CH}_3)_4\text{FeC}_6\text{N}_6$ , and the percentage of iron in a portion that had been recrystallised from chloroform was practically the same as in the unpurified material. It was concluded therefore that the product was homogeneous except for the presence of a small quantity of impurity due to some slight further decomposition taking place during the heating.

\* Through the kindness of Mr. Francis H. Carr we have been enabled to compare the spectrum of norhyoscyamine with that of atropine, and find that there is no difference between them.

Since that time a considerable amount of the compound has been prepared in this laboratory, and it has been possible to study its properties more fully, with the result that an isomeric substance has been isolated in a pure state. For the preparation on a larger scale the following method was adopted. About 30 grams of the chloride, precipitated by ether from an alcoholic solution and dried over sulphuric acid, were heated to between  $140^{\circ}$  and  $150^{\circ}$  in a strong glass retort placed in an air-bath, and exhausted by means of a Fleuss pump. At this temperature gas was freely evolved for about six hours, and in nine hours the evolution had practically ceased. The weight of substance left showed that there was always some decomposition beyond the normal one, and there was invariably a strong odour of isocyanides on opening the apparatus. The contents of the retort were dissolved in about 90 c.c. of hot chloroform, when a pale brown solution was obtained, from which a good crop of crystals, consisting mainly of yellow, rectangular plates, was deposited on cooling. In favourable experiments this crop amounted to nearly 50 per cent. of the substance left in the retort. These crystals contain a large amount of chloroform of crystallisation, which is rapidly given off on exposure to the air, leaving a pale yellow, amorphous powder. This variety will be designated as  *$\alpha$ -tetramethyl ferrocyanide*.

On evaporating the chloroform solution, from which the above crop had been removed, on a hot plate, a white, apparently amorphous substance was gradually deposited—almost completely so by the time the liquid had decreased to about half its original bulk. This solid was best separated by filtration on an “alundum” filter. After it is once deposited, it is practically insoluble in chloroform, but can be purified by crystallisation from hot methyl alcohol, from which it separates on cooling, usually in rather short, yellow needles. This substance, which it is proposed to call  *$\beta$ -tetramethyl ferrocyanide*, constitutes about 5 per cent. of the crude material left in the retort. In a large number of preparations it invariably made its appearance at this stage of the process.

On further evaporation of the chloroform, one or two more crops of the  $\alpha$  compound were obtained, each one becoming more contaminated with impurities, consisting partly of unchanged chloride and partly of some dark substance which becomes blue on drying in the air. Finally, a dark, oily residue, from which no further crystals could be obtained, remained, forming a solid blue mass, when all the chloroform had disappeared. On treating this again with warm chloroform, most of the blue matter remained insoluble, and a further small amount of the  $\alpha$ -variety could sometimes be extracted.

Since the blue substance was found in much larger quantity when the heating of the chloride had for any reason been excessive, it is concluded that it is not a normal product of the reaction, but is formed by some secondary decomposition. It is soluble in water, forming a pale brown solution, which with ferric chloride gives a strong purple coloration. It was not found possible to isolate any pure substance from this residue.

The various portions of the  $\alpha$ -compound were purified by several recrystallisations from chloroform, during which process a very small quantity of the  $\beta$ -variety was occasionally obtained from the later fractions.

An analysis of  $\alpha$ -tetramethyl ferrocyanide made on material crystallised three times from chloroform and heated at  $97^\circ$  until constant gave these results:

0.2618 gave 0.4263  $\text{CO}_2$  and 0.1056  $\text{H}_2\text{O}$ .  $\text{C}=44.4$ ;  $\text{H}=4.5$ .  
0.4952 „ 0.1451  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}=20.51$ .

Analyses of the  $\beta$ -form crystallised three times from methyl alcohol, and also heated at  $97^\circ$  until constant, gave:

0.2283 gave 0.3696  $\text{CO}_2$  and 0.0920  $\text{H}_2\text{O}$ .  $\text{C}=44.2$ ;  $\text{H}=4.5$ .  
0.2503 „ 0.3970  $\text{CO}_2$  „ 0.1018  $\text{H}_2\text{O}$ .  $\text{C}=43.3$ ;  $\text{H}=4.5$ .  
0.2384 „ 0.3830  $\text{CO}_2$  „ 0.0965  $\text{H}_2\text{O}$ .  $\text{C}=43.8$ ;  $\text{H}=4.5$ .  
0.7867 „ 0.2299  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}=20.45$ .

$(\text{CH}_3)_4\text{FeC}_6\text{N}_6$  or  $\text{C}_{10}\text{H}_{12}\text{N}_6\text{Fe}$  requires  $\text{C}=44.09$ ;  $\text{H}=4.47$ ;  
 $\text{Fe}=20.55$  per cent.

The two substances have therefore the same percentage composition within the limits of analytical errors.

*Properties of the two Isomerides.*—The  $\alpha$ -variety is readily soluble in water, methyl alcohol, ethyl alcohol, or chloroform, and insoluble in most of the other usual organic solvents. It separates from concentrated aqueous solutions in very small crystals, which, when dried in the air, contain  $2\text{H}_2\text{O}$ . The water is easily given off either by warming or simply keeping over sulphuric acid in a vacuum. As stated above, it separates from chloroform solutions in large, transparent, rectangular plates, which, however, become opaque so rapidly on exposure to air that no attempt was made to determine the amount of combined solvent.

An aqueous solution gives a red colour with ferric chloride; a white, crystalline precipitate with mercuric chloride, which, when examined under the microscope, is seen to consist of rosettes and bundles of short, rather stout needles; and a very fine, yellow crystalline precipitate with hydrogen platonic chloride. When a fairly concentrated solution is treated with silver nitrate, no immediate precipitate is formed, but after some hours rosettes of white crystals separate. A determination of silver in these agrees with

the formula  $(\text{CH}_3)_4\text{FeC}_6\text{N}_6\text{AgNO}_3$  (Found,  $\text{Ag}=24.28$ . Calc.,  $\text{Ag}=24.39$  per cent.). On heating the  $\alpha$ -compound with methyl iodide, combination takes place, with the formation of  $(\text{CH}_3)_6\text{FeC}_6\text{N}_6\text{I}_2$ . For example, 1.08 grams were heated for six and a-half hours at  $98^\circ$  with excess of methyl iodide in a sealed tube. The solid matter was then found to weigh 2.07 grams. It was first digested with acetone to remove a small quantity of a periodide (which results from the fact that some free iodine is always liberated from methyl iodide vapour by the heat of sealing the tube), and then warm chloroform was added to dissolve out any unchanged tetramethyl compound.

The residue weighed 1.57 grams. It was soluble in water, methyl alcohol, or hot ethyl alcohol. From the latter solvent, on cooling, it was obtained in pale yellow needles:

0.5602 gave 0.0805  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}=10.06$ .

0.3313 „ 0.2795  $\text{AgI}$ .  $\text{I}=45.58$ .

$\text{C}_{12}\text{H}_{18}\text{N}_6\text{I}_2\text{Fe}$  requires  $\text{Fe}=10.07$ ;  $\text{I}=45.61$  per cent.

$\beta$ -Tetramethyl ferrocyanide is soluble in water or methyl alcohol (though far less so than the isomeride), and practically insoluble in ethyl alcohol, chloroform, or other organic solvents. It can be crystallised readily from hot solutions in either of the two first solvents, separating from water in very fine, long, yellow needles containing  $6\text{H}_2\text{O}$ .

In aqueous solution it gives with ferric chloride a red colour similar to that produced by the  $\alpha$ -compound.

It forms a white precipitate with mercuric chloride consisting of very fine, hair-like crystals, and a yellow, insoluble platinumchloride undistinguishable in appearance from its isomeride.

With silver nitrate even in an extremely dilute solution an immediate white precipitate is formed consisting of such fine crystals that they pass through a filter paper. They are soluble in hot water, but separate at once on cooling. By filtering in an "alundum" filter and washing with alcohol, this double salt can be obtained in a suitable condition for analysis, and is found to contain the same percentage of silver as the corresponding  $\alpha$ -compound. (Found,  $\text{Ag}=24.25$ .  $(\text{CH}_3)_4\text{FeC}_6\text{N}_6\text{AgNO}_3$  requires  $\text{Ag}=24.39$  per cent.) Nitric acid precipitates a rather insoluble crystalline nitrate with the  $\beta$ , but none even with a concentrated solution of the  $\alpha$ -form.

Another important point of difference is observed in its behaviour with methyl iodide.

0.65 Gram of the  $\beta$ -form was heated with excess of methyl iodide in a sealed tube under exactly the same conditions as described above with the  $\alpha$ -form. At the end of the experiment the solid



matter had only increased in weight to 0.92 gram, and this increase was evidently due to combination with the free iodine\* (liberated as mentioned above). No trace of the compound  $(\text{CH}_3)_6\text{FeC}_6\text{N}_6\text{I}_2$  was found, and nearly the whole of the original substance was recovered unchanged on recrystallising from hot methyl alcohol.

#### *Determination of the Molecular Weights.*

For this determination a somewhat novel method was employed, since, owing to the rather insoluble nature of the  $\beta$ -variety, a direct measurement of the osmotic pressure was not possible with the apparatus in use in this laboratory, which is not adapted for pressures less than two atmospheres.

In a paper by Lord Berkeley and the author (*Proc. Roy. Soc.*, 1909, A, 82, 271), it was shown that, when an osmotic cell with the membrane deposited as far as possible on the surface of the porcelain is immersed in a solution, the rate at which water is drawn through the membrane is proportional to the osmotic pressure of that solution, if the latter is not too concentrated. By making use of a slight modification of this method, in which the effect produced by solutions of a number of different substances was compared with that of a compound of known molecular weight (in this case sucrose), it was found possible to obtain results from which this constant could be calculated to within  $\pm 3$  per cent. of the true value, and within these limits the molecular weight of  $\alpha$ - and  $\beta$ -tetramethyl ferrocyanide proved to be identical, and to correspond with the simple formula  $(\text{CH}_3)_4\text{FeC}_6\text{N}_6$ .

The details and exact figures of these experiments are not given here, as Lord Berkeley and the author hope shortly to make them the subject of a separate communication.

It seems, then, conclusively proved that two isomeric tetramethyl ferrocyanides exist, having quite distinct properties, although there is a similarity in some of their reactions which suggests that the structural difference is not very great. There is a possibility that the uncrystallisable residue contains one or more further isomerides in small quantity, although so far it has not been found possible to isolate any other pure compounds.

It should be noted here that no indication of isomerism was observed when dealing with the hexamethyl ferrocyanogen salts, several of which were prepared and crystallised in fairly large quantities previous to this work. It must therefore be assumed that the separation into two forms takes place during the heating

\* All the various methylated ferrocyanogen compounds so far described appear to form periodides with free iodine.

of the hexamethylferrocyanogen chloride, since if it were brought about during the subsequent treatment, namely, solution in chloroform, there should be a further deposition of the  $\beta$ -variety to about the same extent on each recrystallisation of the  $\alpha$ -form from that solvent, whereas only very small quantities were ever obtained during this operation, and none at all after the  $\alpha$ -compound had been purified. At present no means have been found to convert one form into the other.

The cases of isomerism hitherto observed in this family of compounds are the  $\alpha$ - and  $\beta$ -ferricyanides discovered by Locke and Edwards (*Amer. Chem. J.*, 1839, **21**, 193, 413), and the  $\alpha$ - and  $\beta$ -ferrocyanides described more recently by Briggs (*T.*, 1911, **99**, 1019). Lately, however, some doubt has been thrown on the existence of the former by Hauser and Biesalski (*Ber.*, 1912, **45**, 3516).

Whether the isomerism of the methylated and metallic ferrocyanides respectively is due to the same cause it is impossible to state, but the differences in chemical and physical properties seem on the whole to be considerably greater in the case of the former, with the exception of the marked difference of colour observed by Briggs in the salts, and not found by the author in the alkyl derivatives. With regard to the nature of the isomerism, Briggs (*loc. cit.*) proposed a modified form of Werner's "co-ordination" system, whilst the author has pointed out (*T.*, 1911, **99**, 1553) that, if one of the ordinary structural formulae, such as Browning's, is adopted, there is the possibility of isomerism due to carbon linked to nitrogen by double bonds, such as occurs in the oximes, etc. However, until more experimental evidence is forthcoming, it appears premature to discuss this point at any length.

With the object of throwing more light on the constitution of the double cyanides, the author is at present investigating the alkyl cobaltcyanides, and has obtained fairly conclusive evidence that these compounds afford another example of isomerism, but the work is not quite complete.

These experiments have been carried out in Lord Berkeley's laboratory at Foxcombe, to whom the author's best thanks are due.

CCXV.—*Solubilities of Salts of Ammonium Bases in Water and in Chloroform. Part I. Solubility as a Constitutive Property.*

By CYRIL JAMES PEDDLE and WILLIAM ERNEST STEPHEN TURNER.

THE measurements recorded in this paper were prompted partly by observations we had previously made in connexion with the relation of the solubility of substances to their state of molecular aggregation (Peddle and Turner, *T.*, 1911, **99**, 685; Turner, *ibid.*, 1911, **99**, 880).

It was pointed out in the second of the two communications referred to that miscibility of two substances was possible when both were normal or both associated, but that solubility was limited when one substance was normal and the other associated; and in support of the rule various illustrations were given, both in connexion with the miscibility of liquids and the solubility of solids in liquids.

In addition to the evidence there quoted, certain other generalisations connecting the properties of molecular weight, solubility, and dielectric constant can be shown to lead to the view that the solubility of a substance should be connected with its degree of association. The first of these generalisations is that of Walden (*Zeitsch. physikal. Chem.*, 1906, **55**, 683) to the effect that the solubility of salts—similar in type to those we have employed—is greater the more highly associated the solvent.

Two other generalisations, taken in conjunction, must also lead at once to the same view. Of these two, the first is also due to Walden (*Zeitsch. physikal. Chem.*, 1908, **61**, 633), and states that the solubility of a normal electrolyte (for example, tetraethylammonium iodide) is greater the higher the dielectric constant of the solvent. This result was established after the examination of thirteen organic liquids, and a quantitative relationship of an empirical character obtained, namely, that the ratio  $\epsilon/\mu$ , where  $\epsilon$  is the dielectric constant of the liquid and  $\mu$ , the molecular solubility of the electrolyte, is a constant quantity.

The second of the two generalisations is the well-known Nerst Thomson rule, which may be stated in the form that the molecular weight of a substance capable of association or dissociation is greater the smaller the dielectric constant (see Turner, *loc. cit.*).

Hence, we expected to find a general connexion between the degree of association of a salt and its solubility in a given solvent.

We may say at once, however, that we have not, under the conditions of experiment described below, been able clearly to establish the connexion we sought.

The data we have adduced, however, furnish information for the solution of several other interesting problems. In the first place, the character of the salts used, derived in many cases either from isomeric bases or from homologues, makes it possible to ascertain whether any additive relationships can be discovered in connexion with solubility, or whether the property is a constitutive one.

Moreover, the discovery of a non-ionising substance, like chloroform, as a solvent for salts is, in itself, important, in that it allows a comparison to be made of the properties of salt solutions in two media of quite opposite character. Walden's work consisted in the examination of but few salts in a large number of liquids. The present investigation, on the other hand, deals with many salts, derived from the substituted ammonium bases and also triethylsulphonium iodide, and only two solvents, water and chloroform. We purpose making a comparison of several properties of solutions in these solvents, contrasting in this first paper the solubility data at a temperature of 25°; whilst in a second communication we hope to give the results of an investigation on the effect of the addition of a second salt on these solubilities.

#### EXPERIMENTAL.

The twenty-four substances used in the investigation include all types of substituted ammonium salts—chlorides, bromides, and iodides—salts of which the molecular weights in chloroform solution have been recorded in a former paper (Turner, *loc. cit.*).

The method of carrying out the solubility determination differed somewhat according as the solvent was water or chloroform. In both cases samples of the salts were thoroughly dried and finely powdered and analysed repeatedly as a check on their purity and freedom from moisture. When water was the solvent, excess of the salt was stirred in a Jena test-tube with water redistilled from acidulated permanganate, until a constant concentration was attained, the temperature variation of the thermostat used being less than 0.1°. The time required to reach constant concentration varied with the salt, but, with one or two exceptions, no measurement was accepted until the solution had been at least twenty-four hours in the bath, and stirred for at least five. As a rule, the time was much longer. A quantity of the solution varying between 2 and 5 grams was then removed to a weighing bottle by means of a pipette, previously warmed to 60–80°, and provided with a plug of cotton-wool at the tip, and the precise weight of solution

determined. After dilution to a known volume, the solution was analysed by Volhard's method by titration with silver nitrate and thiocyanate.

The chloroform used was purified by allowing it to remain for many hours over concentrated sulphuric acid, washing repeatedly with water, drying over calcium chloride, and fractionating to two- or three-hundredths of a degree. Small, brown, stoppered bottles were used for the solubility determinations in chloroform in order to diminish the tendency to decomposition which the bromides and particularly the iodides show when exposed, in this solvent, to the light. The mixture of salt and solvent was warmed to about 40° and then allowed to remain for many hours (twenty-four to one hundred and ten) at 25°, with frequent agitation. The solution, removed and weighed as with aqueous solutions, was placed in a vacuum desiccator, the chloroform slowly removed, and the residue dissolved in water and titrated. With several chlorides, such as propylamine, isobutylamine, and isooctylamine hydrochlorides, which could be heated to 110° without any decomposition, determinations of solubility were also made by evaporation.

The substances are tabulated in series, and the solubility results are expressed under  $P$  as grams of salt dissolved by 100 grams of solvent, under  $100n/N$  as molecular percentage solubility,  $n$  representing molecules of solute,  $N$  of solvent.

In order to avoid repetition at a later stage, we have also inserted in the table the relative degrees of association of the various salts in chloroform solution at the common concentration of 25 milligram molecules per 100 grams of solvent. These factors, denoted by  $A$ , have been drawn from the measurements of one of us (Turner, T., 1911, 99, 880).

The following notes should be made on certain of the solutions.

*Aqueous Solutions.*—Several were slightly coloured through keeping for a prolonged time, the following solutions being slightly yellow or brown: ethylamine and diethylamine hydrochlorides; diethylamine hydrobromide and tetraethylammonium bromide; diethylamine hydriodide; propylamine and dipropylamine hydrochlorides; triethylsulphonium iodide. Solutions of ethylamine hydrochloride and tetraethylammonium chloride were very viscous.

*Tetraethylammonium Iodide.*—Walden (*loc. cit.*) quotes two solubility values, namely, 32.9 and 31.44 grams per 100 grams of solution. Calculated on the same basis, our value is 31.0 grams, corresponding with the lower figure. Since these results, which agree, his and our own, were obtained by employing different processes, the lower number is probably correct.

*Solubilities at 25° in Water and in Chloroform.*

Substance.	M. W.	In water.		In chloroform.		A.
		P.	100g/N.	P.	100g/N.	
NH <sub>4</sub> Cl .....	53.5	39.3	13.24	0.0	0.0	—
NH <sub>4</sub> Et <sub>3</sub> HCl .....	81.5	279.9	61.83	0.17	0.25	—
NH <sub>4</sub> Pr <sub>3</sub> HCl .....	95.5	278.2	52.45	5.26	6.56	(8)
NH <sub>4</sub> Ph <sub>3</sub> HCl .....	109.5	238.9	37.48	11.56	12.63	4.63
NH <sub>4</sub> CH <sub>3</sub> Ph <sub>2</sub> HCl .....	123.6	192.2	28.16	5.10	4.92	5.82
NH <sub>4</sub> Me <sub>2</sub> HCl .....	81.5	369.2	81.57	16.91	24.77	3.92
NH <sub>4</sub> Et <sub>2</sub> HCl .....	109.5	—	38.06	—	—	—
NH <sub>4</sub> Pr <sub>2</sub> HCl .....	37.6	165.3	21.63	47.24	40.98	2.11
NH <sub>4</sub> EtHCl .....	81.5	—	61.83	—	—	—
NH <sub>4</sub> Et <sub>2</sub> HCl .....	109.5	231.7	38.06	29.45	32.09	2.63
NH <sub>4</sub> PrHCl .....	137.6	137.0	17.94	17.37	15.07	1.62
NH <sub>4</sub> PhHCl .....	155.6	141.0	15.35	8.24	5.93	5.12
NH <sub>4</sub> Br .....	97.96	777.0	14.16	0.0	0.0	—
NH <sub>4</sub> Et <sub>3</sub> Br .....	154.0	311.6	36.64	46.65	36.11	—
NH <sub>4</sub> Pr <sub>3</sub> Br .....	182.1	150.6	14.91	23.41	15.37	1.78
NH <sub>4</sub> Et <sub>2</sub> Br .....	210.1	279.5	23.96	25.01	14.21	7.2
NH <sub>4</sub> EtH .....	201.0	377.2	33.79	71.56	42.50	—
NH <sub>4</sub> PrH .....	229.0	370.0	29.09	92.2	48.05	2.52
NH <sub>4</sub> I .....	257.0	45.0	3.15	1.55	0.72	—
NH <sub>4</sub> PhI .....	818.1	18.64	1.07	54.56	20.81	4.40
NH <sub>4</sub> Et <sub>3</sub> I .....	425.3	0.74	0.03	210.8	59.17	2.17
NH <sub>4</sub> Ph <sub>3</sub> HCl .....	129.5	107.1	14.83	—	—	—
NH <sub>4</sub> Me <sub>2</sub> PhCl .....	143.5	378.8	47.54	—	—	—
NH <sub>4</sub> Ph <sub>2</sub> Ph <sub>2</sub> HCl .....	143.5	50.6	0.35	0.0	0.0	—
NH <sub>4</sub> CH <sub>3</sub> Ph <sub>2</sub> HCl .....	233.6	2.17	0.17	0.37	0.19	—
NH <sub>4</sub> CH <sub>3</sub> Ph <sub>3</sub> HCl .....	233.6	0.61	0.03	11.41	4.21	1.26
Et <sub>3</sub> NH .....	246.1	431.0	31.56	47.7	23.14	7.6
C <sub>6</sub> H <sub>5</sub> NEt <sub>3</sub> .....	285.0	301.3	18.99	1.78	0.75	—

\* These values have been obtained from the tables in Seidell's "Solubilities of Inorganic and Organic Substances."

*Tetraisoamylammonium Iodide*.—Solution difficult to titrate unless very dilute.

*Quindine Ethiodide*.—Solution dark red and oily. On addition of water, solution became viscid at first, and a yellow deposit appeared to be formed, but further addition of water gave a clear solution with only a slight yellow tinge.

*Chloroform Solutions*.—Several substances gave yellow or brown solutions, but when evaporated the chloride and bromide residues were usually quite white. Tetraethylammonium iodide, quindine ethiodide, and tetrapropylammonium iodide solutions were deep red.

*Tetraisoamylammonium Iodide*.—Solution light yellow and viscous as glycerol. Solubility determined only by evaporation in a vacuum desiccator (ten weeks required for constancy of weight).

*Benzylamine Hydrochloride*.—No weighable deposit from 7 grams of solution.

*Tribenzylamine Hydrochloride*.—Solubility determined by evaporation, heating to 110°, and placing under diminished pressure.

*Triethylsulphonium Iodide.*—This substance undergoes decomposition in chloroform. A solution of the salt, 0.6074 gram in 5 c.c. of chloroform, was allowed to remain for forty-three hours in the bath, and was then evaporated under diminished pressure, and the residue determined by titration. A loss of 22.2 per cent. of the salt was found to have occurred. Two other solutions, a dilute and a concentrated, were then prepared, and allowed to remain at 25° for half an hour only, after which they were evaporated at the ordinary temperature and under diminished pressure. The first solution contained 0.5040 gram of salt in 6.3568 grams of solution (7.7 per cent.), the second 1.9976 grams in 5.1378 (39 per cent.). The residues determined by titration were 0.5044 gram and 1.990 grams respectively.\* Evidently no appreciable decomposition occurred during the process of evaporation, and the dry salt itself has also been found to be quite stable under diminished pressure at the ordinary temperature. Probably, therefore, the figure quoted in the table does, or very nearly does, represent the actual solubility of triethylsulphonium iodide in chloroform.

#### *Discussion of Results.*

##### *Solubility in Water.*

Great variation is exhibited in the solubilities of the salts, the mono- and di-substituted ammonium chlorides and triethylsulphonium iodide, for example, standing out in marked contrast with di- and tri-benzyl ammonium chlorides or tetraisoamylammonium iodide.

The more important points are summarised as follows:

(1) Substitution of a hydrogen atom in an ammonium salt by an alkyl group very greatly increases the solubility (compare ammonium chloride, ethylamine hydrochloride, propylamine hydrochloride, etc.). Aromatic groups, such as the phenyl or benzyl group, are either much less effective in increasing the solubility or even decrease it. The difference between the aliphatic and aromatic radicles is strikingly brought out by a comparison of aniline with methylaniline hydrochloride, the solubility of the latter being more than three times that of the former.

(2) When similarly constituted salts are compared, solubility in water decreases as the mass increases.

It is only by confining the comparison most strictly to similar substances that such regularity can be observed. The great difference between the effects of aliphatic and aromatic radicles already discussed at once marks solubility as a highly constitutive property.

\* We are indebted to M. C. C. Bissett for making these experiments.

An attempt has been made to test whether any additive relations exist, since the substances examined are so related as make this comparison possible.

Among the chlorides are four pairs of isomeric substances, namely, the hydrochlorides of ethylamine and dimethylamine; of diethylamine and isobutylamine; of triethylamine and dipropylamine; and of methylaniline and benzylamine. Only in one case, the second mentioned, is there agreement between the values of molecular solubility, and in one case there is very wide divergence. Lack of agreement between isomerides, however, does not necessarily mean the absence of any additive relationships, as is well known. Comparing the homologues in the first three series in the table of solubilities, neglecting ammonium chloride, and making no comparison between *n*-propylamine and isobutylamine hydrochlorides, we have as differences between the members compared, in the first series 9.38 and 9.32; in the second, between salts of secondary amines,  $2 \times 21.75$  and  $2 \times 8.2$ ; in the third,  $2 \times 11.3$ ,  $2 \times 10.1$ , and  $2 \times 1.3$ . These differences in the molecular solubility, set out in terms of a difference of composition of  $\text{CH}_2$ , do not raise any great hope of discovering additive relationships, although the persistent recurrence of an average difference value of about 9 units may not be without significance.

Whatever the outcome of further and more exhaustive investigation of substances of precisely similar constitution, it is obvious that the solubility of salts in water must be written down as almost wholly, if not wholly, a constitutive property.

(3) The constitutive character of solubility is also borne out in the effect exercised by the negative radicle, and it is not possible to say definitely whether the chloride, bromide, or iodide will have the greatest solubility in water.

#### *Solubility in Chloroform.*

Compared in the usual sense (values of  $P$ ), the salts appear to be distinctly less soluble in chloroform, on the whole, than in water. The surprising thing is that they are so soluble. In most other organic solvents of low dielectric constant, such as ether, benzene, carbon disulphide, carbon tetrachloride, and ethylene dibromide, their solubilities are exceedingly small, and from experiments we have carried out they are much more soluble in chloroform than in acetone. The magnitude of the solubility is all the more striking when reduced to terms of molecular solubility, when the numbers, taken as a set, are but little less than in water as solvent. Solubility in chloroform is therefore exceptional. It does not appear to depend on the fact that all the salts used in this investi-



gation are haloids, for, from the experience of one of us, nitrates are likewise very soluble, and so also are various other salts containing still other negative radicles. There is no doubt that in this respect chloroform is a somewhat exceptional although at the same time a valuable solvent. Compared with water, it is often to be found that the greater the solubility in water the smaller it is in chloroform, and vice versa; but there are quite a number of exceptions. It is obvious that in comparing a series of salts, a point will be reached at which solubility in water and in chloroform will be nearly the same. This applies in all probability to the triethylamine salts, possibly also to those of diethylamine, the solubilities of which in chloroform appear exceptionally high. Other points to which attention may be called briefly are:

(1) As in water, so also in chloroform, the solubility of an ammonium salt is greatly increased by the introduction of organic radicles, the aliphatic again having a much greater effect than the aromatic. Although we have made no exact measurements with aniline and methylaniline hydrochlorides, we have found that the former may be regarded as insoluble, whilst the latter is very soluble in chloroform.

(2) As a rule, increase in molecular weight is accompanied by increase of solubility. This rule is only strictly preserved when series of similarly constituted salts are compared (compare, for example, the monoalkylamine and dialkylamine salts as two series, as also the tetraethyl-, propyl-, and *iso*amyl-ammonium iodides).

*iso*Amylamine hydrochloride is an exception even under these conditions.

(3) No suggestion of additive relationships occurs either by a comparison of isomerides or of homologous substances.

(4) With the exception of tetraethylammonium iodide, the order of increasing solubility is chloride, bromide, iodide, so far as investigated.

The absence of any definite connexion between solubility in water and in chloroform and chemical composition of the above salts may well give rise to the question as to whether any physical property of either component of the solution may affect the extent to which miscibility may occur, and this leads back to one of the objects of the investigation, namely, the effect of molecular association on solubility.

It is very possible that this factor has an influence. In the solid state these salts must be regarded as built up of complex molecules; in aqueous solution they appear dissociated, in chloroform strongly associated. Now in accordance with the rule mentioned in the

introduction, that two substances which are both associated will readily mix, it should be found that the strongly associated salts should be the ones most soluble in water. A strict test of the rule requires a knowledge of the molecular state of the salt in saturated solution, and this is not known except in a few cases. The association factors for dilute solution do largely indicate the relative order of complexity for much stronger solutions, however, and, recognising this, the table on p. 1205 shows that the rule holds, generally speaking, although the order of association is in many cases not that of solubility. As to solubility in chloroform, it can be pointed out that when similarly constituted salts, such as the monosubstituted amine salts, the disubstituted salts, and the tetraalkylammonium iodides are compared in series, then the solubility increases as the degree of association decreases. Some doubt may be felt as to the sufficiency of this illustration, and in view of the fact that the iodides, the most associated salts, are in several cases nevertheless the most soluble, it must be admitted that molecular association cannot be the deciding factor in solubility. That it is a factor is probable from what has been said already, and in the series of monoalkylamine hydrochlorides, *is*amylamine hydrochloride is abnormal in being more associated than *isobutyl*amine hydrochloride, and, in conjunction with this, also has the smaller solubility, which is also abnormal. If it be admitted that molecular association is a factor affecting solubility, it is not unlikely that if a solvent like ethyl alcohol be employed, which, one of us has found, neither permits either marked association nor ionisation, greater regularity might be found to exist among the solubilities observed.

We hope further to discuss this point in a later communication, and to examine in some detail the relationship between solubility and dielectric constant and between dielectric constant and molecular weight, which, as already indicated in the introduction, suggest the connexion between molecular state and solubility.

We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed much of the expense entailed by this investigation.

THE GRAMMAR SCHOOL,  
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THE UNIVERSITY,  
SHEFFIELD.

CXXVI.—*The Mode of Combustion of Carbon: the  
Effect of Drying the Oxygen.*

By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER, ARMSTRONG and Colgate, in a recent paper (*J. Soc. Chem. Ind.*, 1913, **32**, 391), have suggested that water (as an electrolyte) plays an all-important part in determining the manner in which carbon burns.

The experiments recorded in our paper, "The mode of combustion of carbon" (this vol., p. 461), wherein we advanced a hypothesis that the first reaction between oxygen and carbon results in the formation of a loosely combined "physico-chemical complex," were made with air or oxygen dried by contact for several days with concentrated sulphuric acid. We also made a number of experiments with air dried by contact with phosphoric oxide, the results of which were not recorded in that paper, but of which a record seems desirable.

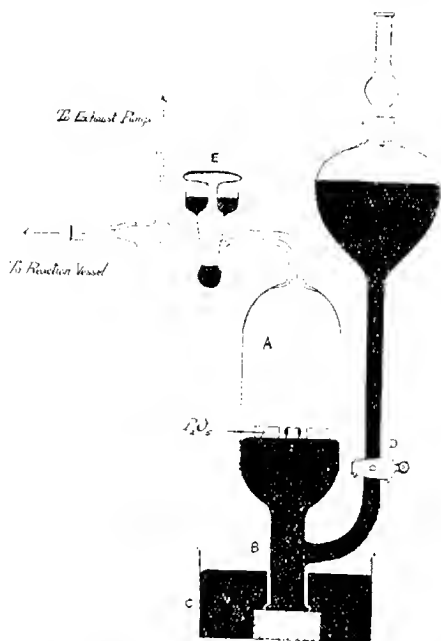
H. B. Baker, in his work on combustion in dried oxygen, referred to in our previous papers, used purified sugar charcoal, which, from the details of the experiments given, appears to have been "saturated" with oxygen at a low temperature before being raised to the experimental temperature.

The most striking result of his experiments, apart from the difficulty with which the dried oxygen combined with the carbon, was the large proportion of carbon monoxide found in the products of combustion. Thus, when oxygen which had been dried by contact with phosphoric oxide during three weeks was passed over carbon contained in a hard glass tube and heated to bright redness with a gas blowpipe, no visible combustion occurred, and the gases that passed over had the following percentage composition:

Carbon dioxide.....	2.2
Carbon monoxide.....	39.5
Oxygen.....	58.1

It being well known that dried oxygen and carbon monoxide unite with great difficulty, Baker naturally contended that since this method of rendering the conditions unfavourable to the oxidation of carbon monoxide resulted in the production of an increased quantity of that gas when carbon was burnt, one is justified in regarding it as, in all probability, the first product of combustion. By this, we believe, he intended to convey the suggestion that carbon monoxide is the "first product" so far as carbon dioxide is concerned—that it does not arise from reduction

of carbon dioxide; but that all, or most, of the carbon dioxide found in the products of combustion of carbon by "moist" oxygen at a bright red heat arises from the subsequent oxidation of carbon monoxide; for his results in no way preclude the possibility of the preliminary formation of a complex or compound other than carbon monoxide or carbon dioxide. On the contrary, if our hypothesis regarding the mode of combustion of carbon is correct, Baker's



experiments should afford information regarding the ratio in which carbon dioxide and carbon monoxide appear as the decomposition products of the "complex" at different temperatures; for the extreme dryness of the oxygen would prevent its reaction with carbon monoxide, and would thus "fix" or "freeze" the ratio.

It is necessary, however, to consider whether dryness of the oxygen affects in any way the formation of the "complex." To determine this we have made pairs of experiments with dried and undried air in the following manner.

The quartz bulb employed for the fixation experiments described in our previous paper (*loc. cit.*, p. 473) was used as the reaction vessel, and a gasholder for drying the air over phosphoric oxide was attached by a ground joint. This gasholder had the form shown in the diagram. The gas reservoir *A* was filled with freshly boiled and distilled mercury, the wide tube *B* being open and standing over mercury in the trough *C*, and the tap *D* leading to the mercury reservoir being closed. Dry air was then passed up under the mercury in the trough until the reservoir was about three parts full, and eight or nine plugs of freshly purified phosphoric oxide were introduced. The wide entrance tube was then closed under the mercury in the trough by a rubber pad, and the apparatus left for several weeks.

Before making the experiment the reaction tube was heated to 1100°, and exhausted during forty-eight hours at that temperature. The temperature was then lowered to the experimental temperature, and the dried air introduced to the vacuum reaction vessel by quickly opening the mercury-cup tap *E*, the tap *D* leading to the reservoir of dry mercury being opened.

Heating was continued during a given length of time, and the residual gases then pumped out.\* The temperature of the carbon was then raised to 1100°, and the gases evolved were collected.

The following are typical results:

Duration of heating.	Temperature 200°.		
	Undried air, 10 mins.	Air dried during 4 weeks over phosphoric oxide.	
		10 mins.	5 h. 4 m.
Residual gas †: volume c.c. ....	22.79	24.87	25.33
Analysis CO <sub>2</sub> .....	2.45	2.30	2.15
O <sub>2</sub> .....	nil	nil	nil
CO .....	nil	nil	nil
Gas evolved at 1100° ‡: volume c.c. ....	9.47	9.74	10.06
Analysis CO <sub>2</sub> .....	10.55	12.65	12.29
O <sub>2</sub> .....	nil	nil	nil
CO .....	89.10	84.85	87.35
Oxygen burned, c.c. ....	5.87	6.05	6.17
Percentage of oxygen burned appearing as:			
CO <sub>2</sub> .....	9.6	9.1	8.8
CO .....	nil	nil	nil
" C <sub>2</sub> O <sub>2</sub> " .....	90.4	90.6	91.2

A temperature as low as 200° was chosen because we wanted, if possible, unburned oxygen to remain at the end of the experiments, whether the air was dried or undried. For the same reason

\* A phosphoric oxide drying tube was fused between the Sprengel mercury pump and the reaction vessel.

† Termed "final gas" in our previous paper.

‡ Termed "C<sub>2</sub>O<sub>2</sub> gas" in our previous paper.

the duration of heating was made as short as the experimental method would allow.

It will be seen that there is practically no difference between the results of the experiments with dried air and that with undried. No measurable quantity of carbon monoxide was present in the gases that remained over the carbon at 200°, nor was there any unburned oxygen.

We conclude from these experiments that the formation of the "complex" is in no way prevented by the drying of the oxygen. It would appear therefore that its decomposition is accelerated by the presence of moisture, for Baker has clearly shown that moisture (to the extent that would be present in air dried by concentrated sulphuric acid) accelerates the "combustion" of carbon—accelerates the formation of carbon monoxide and carbon dioxide. If, as we assume, these two gases arise from the decomposition of a complex first formed, and there is no retardation in the formation of the complex by drying, it must follow that its decomposition is prevented or minimised by the absence of moisture.

In this connexion it may be recalled that C. J. Baker (T., 1887, 51, 249) found that after well-dried oxygen had been admitted to purified carbon at a low temperature ( $-12^{\circ}$ ), only traces of gas (carbon dioxide) were evolved on heating to 150°, or by stages of 50° up to 350°. On raising the temperature to 450°, however, a slow but regular evolution of gas (mainly carbon monoxide) took place.

Circumstances prevent us at present from pursuing further the question of the influence of moisture, or it would have been of interest to have repeated the series of "fixation" experiments recorded in our previous paper, using air dried by phosphoric oxide. For, as already suggested, by preventing or retarding the combustion of carbon monoxide by this means, a nearer approach to the true ratio in which carbon dioxide and carbon monoxide arise from decomposition of the complex would be obtained than by relying, as we did in our experiments with "undried" air, on the rapid removal of the oxygen from the sphere of action by "fixation."

One experiment with air dried over phosphoric oxide during sixteen days, and admitted to purified carbon at 300°, can be compared with the corresponding experiment with "undried" air given in our previous paper.

*Dried Air at 300°.*

Duration of heating.	30 minutes.
"Final gas" : volume c.c. ....	19.87
Analysis CO <sub>2</sub> .....	4.10
O <sub>2</sub> .....	nil
CO .....	0.50
"C <sub>2</sub> O <sub>2</sub> gas" : volume c.c. ....	6.84
Analysis CO <sub>2</sub> .....	11.20
O <sub>2</sub> .....	nil
CO .....	88.40
Oxygen burned, c.c. ....	4.85
Percentage of oxygen burned appearing as :	
CO <sub>2</sub> .....	17.6
CO .....	1.1
C <sub>2</sub> O <sub>2</sub> .....	81.3

This result differs in no important respect from that of the corresponding experiment with undried air (*loc. cit.*, p. 476). The ratio CO<sub>2</sub>/CO in the "final gas" is 8.20 in the "dried," as compared with 8.60 in the "undried" experiment.

ESKMEALS.

## CXXVII.—*Studies of Dynamic Isomerism. Part XV.* *The Influence of Light on Isomeric Change.*

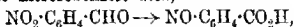
By THOMAS MARTIN LOWRY and HAROLD REUBEN COURTMAN.

THE isomeric changes which have been studied in previous papers of this series have been shown to be exceedingly sensitive to the influence of various chemical agents. A climax was probably reached when it was found that the stimulating influence of piperidine on solutions of nitrocamphor in benzene could still be detected at a dilution of 1 part in 100 millions, or 1 centigram per 1000 kilos. Carbonyl chloride, on the other hand, as a natural impurity in chloroform or an added impurity in other solvents, was capable of arresting this isomeric change by eliminating basic impurities in the form of inactive carbamides; in the presence of this "anti-catalyst" an absolute arrest of isomeric change was maintained, in one instance at least, during a period of nearly a month.

Under these conditions it was a matter of great interest to find out how these very sensitive changes would be influenced by exposing the solutions to a powerful light.

Such experiments were the more important in view of the remarkable influence exerted by light upon the relatively sluggish change

of maleic into fumaric acid in presence of bromine (Bruner, *Bull. Acad. Sci. Cracow*, 1910, 192), and of *allocinnamylidenecacetic acid*,  $C_6H_5 \cdot CH:CH \cdot CH_2 \cdot CO_2H$ , into its more stable stereoisomeride in the presence of iodine (Liebermann, *Ber.*, 1895, 28, 1438, 1443). These changes do not usually take place at all except in the presence of a large quantity of an added catalyst, such as concentrated hydrobromic acid; the readiness with which they take place on exposure to light indicates that this may provide a very powerful weapon for promoting change. This conclusion is supported by the fact that the internal oxidation-reduction of nitrobenzaldehyde to nitrosobenzoic acid,



is readily effected by exposure to light, even when the substance is in the solid state.

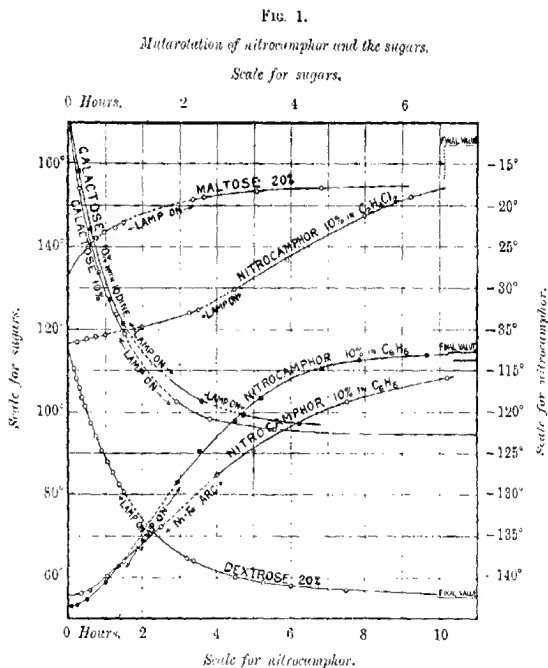
About ten years ago, when silica glass was first introduced, attempts were made to study the influence of ultra-violet light on some of the more facile isomeric changes, by exposing a solution in a silica polarimeter tube to the light of an arc. It was soon realised, however, that trustworthy conclusions could only be drawn if the solution was maintained at constant temperature. The rapid progress which has been made in the production of silica apparatus, together with the development of the silica-mercury lamp, has now made it easy to carry out critical experiments by methods that would have been impossible a few years ago. The observations now described were carried out with the help of a silica-jacketed, silica polarimeter tube (*Trans. Faraday Soc.*, 1913, 8), through the outer jacket of which distilled water, at a constant temperature of  $20^\circ$ , was circulated. The solution in the inner tube, protected in this way from purely thermal influences, was exposed to dazzling radiation from a silica mercury lamp (*Trans. Faraday Soc.*, 1912, 7, 269, Fig. 2), running parallel to the central tube and at a distance of about 5 cm. from it. The radiation, which was much more powerful than sunlight, and contained a wide range of brilliant ultra-violet rays, was generally allowed to act on the solutions for an hour at a time. During this period no polarimetric readings could be taken, but by tracing the course of the mutarotation curve before and after exposure to light, it was easy to see whether isomeric change had been stimulated in any degree by this powerful "insolation."

*The Sugars.*—The three sugars selected for examination were dextrose, galactose, and maltose. The two former were highly purified specimens which had been soaked in a mixture of alcohol and water during eight years in order to convert them wholly into the least soluble form. The maltose was a commercial specimen.



Each sugar was examined in an aqueous solution; the galactose was also examined in an aqueous solution, to which iodine had been added. The four curves reproduced in Fig. 1 indicate the limits of the change of rotatory power when mercury green light of wave-length 5461 is substituted for sodium light. The four curves agree in showing not the slightest acceleration by exposure to the light of the mercury arc.

*Nitrocamphor.*—This substance was examined both in ethylene

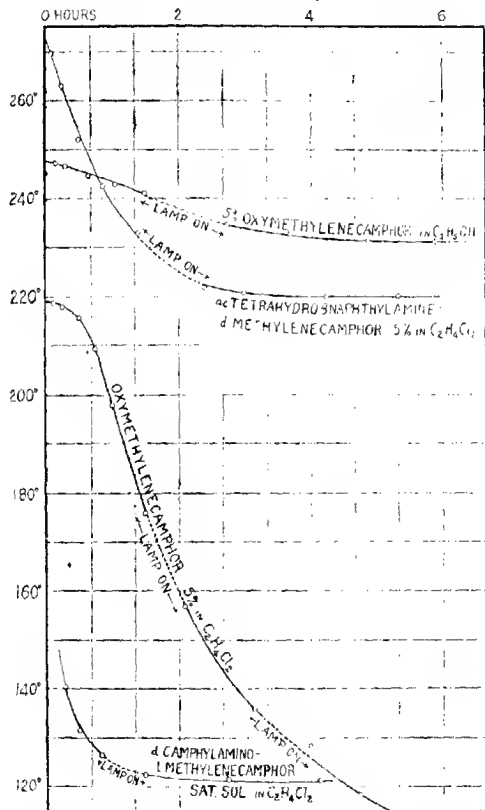


chloride (which had not been used previously for this purpose) and in benzene, these solvents being selected as typical diatonic and absorbent media. The solution in benzene was exposed to the light of an iron-nickel arc, which gives a very crowded line-spectrum, as well as to the light of the mercury arc, which gives a more open spectrum containing a smaller number of very powerful lines. The

three curves shown in Fig. 1 again show no acceleration whatever.

*Hydroxymethylenecamphor*.—This substance could only be used

FIG. 2.  
*Isomerization curves for hydroxymethylenecamphor and its derivatives.*



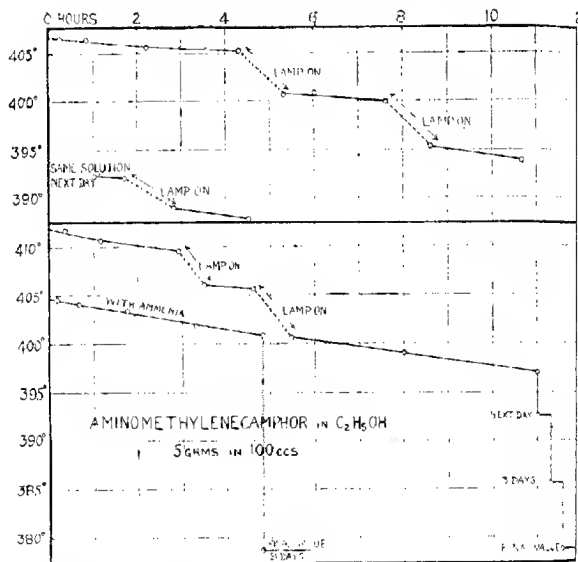
after it had been distilled in a current of steam in order to remove acid impurities, thus reducing the velocity of isomeric change to within reasonable limits. It was examined in alcohol, where the

change of rotation is very small, and in ethylene chloride, where the range is very large. Negative results were again obtained, as also in the case of two amino-derivatives prepared by Prof. Pope, for which curves are given in Fig. 2.

*Aminomethylenecamphor.*—These negative results are the more remarkable in view of the striking effects produced in the case of the closely related aminomethylenecamphor by exposure to light under precisely similar conditions. The curves shown in Fig. 3

FIG. 3.

*Influence of light on the mutarotation of aminomethylenecamphor.*



need very little explanation. The normal rate of change was slow, so that even after a day had elapsed the change was still far from complete; the addition of ammonia exerted only a very slight catalytic action. On exposure to light, however, the substance immediately responded by changing with great rapidity. On removing the stimulus, the change reverted to its original slow rate, but could be accelerated again by a further exposure to light. A rapid change could be induced in this way even when the slower

change had been proceeding during a whole day. The vertical dotted lines in the lower part of the figure are not mutarotation curves, but are used merely to link together observations made on different days.

*$\alpha$ -Benzoylcamphor.*—Special interest attaches to this substance, in reference to the "enolic" form of which Forster (T., 1901, 79, 1001) writes that "On exposing a freshly prepared solution to sunlight, the rapidity of the change becomes greatly exaggerated, the position of equilibrium being reached in two or three hours," instead of in six days. Attention was directed at the same time to the stability of the colourless crystals of the enolic isomeride, "a solution in chloroform having been preserved in darkness during twelve hours, exposed to bright sunlight during two hours, and even sown with a crystal of the ketonic isomeride, without suffering any perceptible reduction in optical activity." It is very probable that, as in the case of nitrocamphor, carbonyl chloride was here acting as an "anti-catalyst," and producing an arrest of isomeric change.

Attempts to study the action of light on this substance when dissolved in ethylene chloride were abandoned on account of the steeply inflected character of the mutarotation curve. But when using chloroform as the solvent, the inflexion disappears, and the curve resumes a normal appearance. We were fortunate in obtaining a specimen which changed very slowly, so that the action of light was easily detected. The results obtained were remarkable, and differed completely from those observed in the case of amino-methylenecamphor. Exposure to light at once stimulated the isomeric change, but the effects of the stimulus persisted after the light had been extinguished, so that the course of the curve was permanently deflected.\* This acceleration was shown three times over on the same curve by repeated exposure of the solution to light (Fig. 4).

As it seemed possible that the permanent stimulus might be due to the liberation of a catalyst (say hydrogen chloride) from the chloroform used as solvent, the experiment was repeated with benzene as solvent, the readings being taken in this case with green mercury light. Precisely similar effects were observed. A solution which had not been exposed to light showed a very slow change of rotatory power. A second portion of the same solution showed the same initial rate of change, but was so stimulated by exposure to light during a period of forty minutes that the mutarotation was practically complete at the end of two more hours.

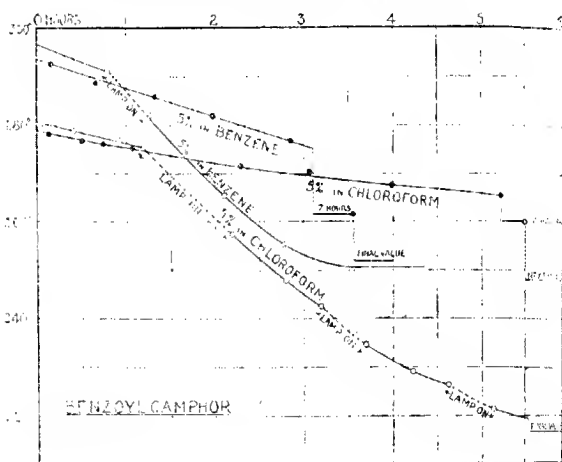
In the last experiments the only elements present in solvent and

\* These curves were plotted for sodium light as in Forster's experiments; all the others are for mercury-green light, wave length 5461.

solute were carbon, hydrogen, and oxygen. The catalyst produced by the action of light must therefore be some purely "organic" compound, for example, an organic acid or ketone. Experiments in which benzoic acid was added to solutions of (enolic) benzoylcamphor in benzene showed a remarkable catalytic effect, the change being completed in about twenty minutes in the presence of a quantity of benzoic acid amounting only to 1 gram per litre of solution, or 2 per cent. of the weight of the solute. It is therefore

FIG. 4.

*Influence of light on the mutarotation of benzoylcamphor.*



very probable that the action of light on benzoylcamphor sets free small quantities of benzoic acid, and that the permanent stimulus to the isomeric change is due to the presence of this substance in the solutions.

#### *Summary.*

1. Ultra-violet light does not accelerate the isomeric change of dextrose, galactose, or maltose, of nitrocamphor, or of hydroxymethylenecamphor.
2. In the case of aminomethylenecamphor there is a marked acceleration, which ceases when the stimulus is removed.
3. Benzoylcamphor also undergoes isomeric change more rapidly

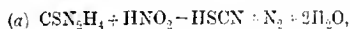
in presence of light, but the acceleration persists after the light has been withdrawn. The permanent stimulus is probably due to the liberation of benzoic acid, which acts as a powerful catalyst in promoting isomeric change.

CXXVIII.—*The Estimation of Nitrites by means of Thiocarbamide, and the Interaction of Nitrous Acid and Thiocarbamide in the Presence of Acids of Different Strength.*

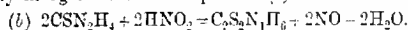
By MAY EMILY COADE and EMIL ALPHONSE WERNER.

IN a recent communication (Werner, T., 1912, 101, 2180) it was pointed out that when a nitrite is added to an acid solution of thiocarbamide, the reaction may proceed in two directions, dependent entirely on the relative strength or ionising power of the acid present.

Thus, in presence of a feeble ioniser, such as acetic acid, the change takes place almost entirely in accordance with the following equation:



whilst if hydrochloric acid is present, the change is almost theoretically in agreement with equation (b):



In reaction (a) a small quantity of nitric oxide is always produced, and in reaction (b) the evolved gas contains a small proportion of nitrogen; this is of no importance so far as the estimation of nitrites is concerned, since the total volume of gas evolved is the same in both cases.

A few preliminary experiments seemed to indicate that thiocarbamide was likely to prove a useful substance for the estimation of various nitrites, and the results now recorded show beyond question that we have in this compound an admirable reagent for the simple, rapid, and accurate estimation of all nitrites by a gasometric method.

In carrying out these analyses, the following procedure was found to give very satisfactory results: a quantity of the nitrite, corresponding with a milligram-molecular proportion of nitrous acid together with 0.1 gram of thiocarbamide, was dissolved in 1 c.c. of water in the cup of the nitrometer, and introduced into

the apparatus; an additional  $\frac{1}{2}$  c.c. of water was used to wash in the last traces from the cup; 1 c.c. of dilute acetic acid (20 per cent.) was then added. The reaction was completed in a few minutes. On account of the somewhat greater solubility of nitric oxide in water, as compared with nitrogen, it is preferable to use acetic acid.

A test experiment with pure silver nitrite gave a result in agreement with the theoretical; a sample of sodium nitrite gave for the mean of seven closely agreeing results a value equal to 96.76 per cent. of pure sodium nitrite; the same sample, when analysed by the well-known method, using ordinary carbamide, gave only 93.89 per cent. of pure sodium nitrite for the mean of three experiments, which were by no means so concordant as when thiocarbamide was used (Expts. 1—10).

An elegant volumetric method for the estimation of nitrites has been proposed by Rupp (*Zeitsch. anal. Chem.*, 1906, **45**, 690), based on the oxidation of the nitrite by a feebly alkaline solution of potassium permanganate, the excess of the latter, after five to ten minutes' heating on the water-bath, being determined by addition of potassium iodide, and after acidification, titrated with N/10-sodium thiosulphate. Two analyses of the sample of sodium nitrite by this method gave a mean value equal to 96.75 per cent. of pure nitrite, thus confirming the results obtained by the thiocarbamide method.

Estimations of ethyl nitrite in alcoholic solution have given results which appear to be more trustworthy than when the potassium iodide method is employed; with thiocarbamide, the values obtained were found to be always lower than those yielded by potassium iodide. This is due apparently to the presence of some nitric ester in the ethyl nitrite solution, which has a disturbing influence on the results obtained by the latter method, since a greater divergence was found in the values obtained from the analyses of an old specimen of the nitrous ester; the results of experiments 19 and 20 also appear to confirm this view.

The advantages which may be justly claimed for the estimation of nitrites by the aid of thiocarbamide are as follows:

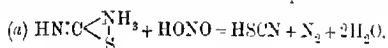
- (1) The accuracy of the results is not affected by the presence of nitrates, even when in large excess.
- (2) The analysis can be completed in a few minutes, since no subsequent manipulation of the evolved gas is necessary, as in the case when ordinary carbamide is used; this also reduces the chances of experimental error.
- (3) The volume of gas evolved can be read off with great accuracy, since the operation is remarkably clean; even after a

large number of analyses the mercury remains quite untarnished, a result which is in marked contrast to that which occurs when potassium iodide is used after even a single operation.

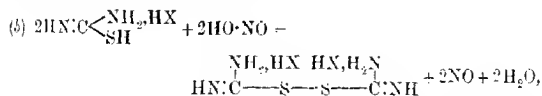
(4) For the reasons given in (2) and (3), a much larger number of analyses can be made in a given time than by the other methods. For example, in the presence of sulphuric acid, the reaction is completed in about forty-five seconds; using acetic acid, it required only two minutes; in a comparative test, using carbamide in presence of sulphuric acid, the evolution of gas was not completed until after a lapse of twenty-eight minutes.

*The Influence of Different Acids on the Composition of the Evolved Gas, when Nitrous Acid and Thiocarbamide interact.*

The following results furnish interesting confirmatory evidence in support of the theory which has recently been put forward by one of us (Werner, *loc. cit.*) to explain the sharp difference in the behaviour of nitrous acid towards thiocarbamide under the two conditions already referred to. In a neutral solution the thiocarbamide molecule is in a state of fairly stable equilibrium, represented by the configuration  $\text{HN}:\text{C} \begin{smallmatrix} \text{NH}_3 \\ \diagup \\ \text{S} \end{smallmatrix}$ , which is not disturbed by the presence of a feeble ioniser, such as acetic acid, with the result that the nitrous acid exerts a direct oxidising action on the thiocarbamide in accordance with the equation:



When a strong acid is added, a salt of thiocarbamide is at once formed of the structure  $\text{HN}:\text{C} \begin{smallmatrix} \text{NH}_2, \text{HX} \\ \diagup \\ \text{SH} \end{smallmatrix}$ , and oxidation by nitrous acid then takes place as follows:



According to this view, the relative proportions of the two gases evolved should indicate the extent to which a particular acid was capable of reacting with thiocarbamide to form a salt, since interactions (a) and (b) will proceed simultaneously when both configurations of the thiocarbamide molecule are present in the solution.

In all the experiments, equal molecular proportions of thiocarbamide and sodium nitrite with two molecular proportions of the acid were allowed to interact in the same volume of solution;



the concentration of the thiocarbamide was therefore the same in each case; that of the acid varied somewhat according to the difference in molecular weight. For the latter reason it may be rightly argued that the experiments are not strictly comparable; still, the results recorded below prove conclusively that the direction of the change on the lines of equation (b) is directly proportional to the dissociation constant of the acid, a strong fact in support of the explanation just stated. The values in tables I and II have been calculated from the data given in the experimental part of this paper.

TABLE I.

	NO. per cent.	N <sub>2</sub> per cent.		NO. per cent.	N <sub>2</sub> per cent.
Hydrochloric acid .....	95.95	4.05	Lactic acid .....	35.21	64.79
Oxalic acid .....	88.66	11.34	( $K=0.0147$ )		
( $K=10$ )			Glycollic acid .....	32.51	67.49
Tartaric acid .....	59.01	41.99	( $K=0.0152$ )		
( $K=0.103$ )			Succinic acid .....	19.37	80.63
Malonic acid .....	51.88	48.12	( $K=0.00653$ )		
( $K=0.163$ )			Acetic acid .....	12.55	87.45
Malic acid .....	39.68	60.32	( $K=0.0018$ )		
( $K=0.0336$ )			Propionic acid .....	11.60	88.40
			( $K=0.0013$ )		

TABLE II.

	NO. per cent.	N <sub>2</sub> per cent.		NO. per cent.	N <sub>2</sub> per cent.
<i>o</i> -Bromobenzoic acid ...	31.77	68.23	<i>o</i> -Nitrobenzoic acid ...	25.98	74.02
<i>m</i> -Bromobenzoic acid..	18.16	81.84	( $K=0.010$ )		
( $K=0.01307$ )			<i>m</i> -Nitrobenzoic acid ...	12.48	87.52
<i>p</i> -Bromobenzoic acid...	0.0	100.00	( $K=0.035$ )		
			<i>p</i> -Nitrobenzoic acid ...	4.35	95.65
			( $K=0.039$ )		

With the above derivatives of benzoic acid, it was necessary to use a certain amount of alcohol to help the solution of the acids, and in the case of the *p*-derivatives a larger volume was required than for the *o*- and *m*-compounds; the ionisation being thereby greatly diminished all round, the change has been diverted in the direction of equation (a) out of proportion to the dissociation constants of the acids. The larger volume of alcohol required in the case of *p*-nitrobenzoic acid, as compared with the *meta*-derivative, is no doubt the cause of the wide difference in the two results, which is also magnified by the influence of concentration, a factor the effect of which has yet to be studied. The result with *p*-bromobenzoic acid is remarkable as the only case in which nitrogen only was obtained; no record of its dissociation constant could be found.

Difference in concentration is probably also responsible for the order of the values obtained for malonic and tartaric acids, although the difference in constitution may also have some effect. It is intended to carry out further experiments to test these points.

### EXPERIMENTAL.

#### *Estimation of Nitrites by means of Thiocarbamide.*

In order to establish the accuracy of the method, a specimen of freshly prepared silver nitrite, purified by recrystallisation from hot distilled water, was analysed, with the following result:

Silver nitrite (M.W. 153.9: 0.07695 gram) and thiocarbamide (0.1 gram) were introduced into the nitrometer with 2 c.c. of water, and 1 c.c. of acetic acid (20 per cent.) was added.

Vol. of gas evolved = 12 c.c. at 16.7° and 769.8 mm. = 11.24 c.c. (dry) at 0° and 760 mm.

Theoretical volume at N.T.P. = 11.18 c.c.

One gram of hydrogen, at N.T.P. = 11.18 litres, has been taken as the standard throughout all the experiments.

#### *Analyses of Sodium Nitrite alone, and in the presence of Different Proportions of Sodium Nitrate.*

A sample of commercial pure fused sodium nitrite was used. 0.069 Gram of the sample and 0.1 gram of thiocarbamide were dissolved in 2 c.c. of water, and having been introduced into the nitrometer, 1 c.c. of dilute acetic acid (20 per cent.) was added. The reaction was completed in a few minutes. Theoretical volume of gas at N.T.P. = 22.36 c.c.:

	Vol. at N.T.P. in c.c.	NaNO <sub>2</sub> per cent.
Expt. 1:		
Gas evolved 23.5 c.c. at 17.4° and 758.82 mm. ....	21.64	96.84
Expt. 2:		
Gas evolved 23.5 c.c. at 16.6° and 757.5 mm. ....	21.66	96.87
Expt. 3. 0.2 gram NaNO <sub>3</sub> present:		
Gas evolved 23.8 c.c. at 17.6° and 750.5 mm. ....	21.66	96.87
Expt. 4. 0.3 gram NaNO <sub>3</sub> present:		
Gas evolved 23.4 c.c. at 16.7° and 760.35 mm. ....	21.65	96.82
Expt. 5. 0.4 gram NaNO <sub>3</sub> present:		
Gas evolved 23.9 c.c. at 18.8° and 750.55 mm. ....	21.61	96.64
Expt. 6. 0.6 gram NaNO <sub>3</sub> present, also in Expt. 7:		
Gas evolved 23.2 c.c. at 14.6° and 757.9 mm. ....	21.61	96.64
Expt. 7:		
Gas evolved 23.4 c.c. at 15.9° and 756.7 mm. ....	21.62	96.69

The presence of nitrates therefore does not materially affect the accuracy of the method, even when present to the extent of ten times the amount of the nitrite. This result is of importance in connexion with the use of thiocarbamide as a reagent for the

estimation of nitrous esters, such as ethyl and amyl nitrites, which are liable to contain some of the corresponding nitric ester.

*Comparative Analyses of the same sample of Sodium Nitrite by means of Carbamide.*

0.069 Gram of the sample of nitrite and 0.1 gram of carbamide were dissolved in 2 c.c. of water, and 1 c.c. of dilute sulphuric acid (1 in 7) was added; after absorption of the carbon dioxide by 1 c.c. of 30 per cent. potassium hydroxide solution, the following results were obtained:

	Volume of gas ( $N_2$ ).	Vol. at N.T.P. in c.c.	$NaNO_2$ per cent.
Expt. 8.	22.9 c.c. at $13.2^\circ$ and 733 mm. ....	20.74	92.75
Expt. 9.	22.6 c.c. at $14.6^\circ$ and 749.6 mm. ....	20.81	93.07
Expt. 10.	23.0 c.c. at $14.1^\circ$ and 733.5 mm. ....	20.76	92.84
Mean of thiocarbamide results = 96.76 per cent. $NaNO_2$ .			
,, carbamide ,, = 92.89 ,, ,,			

The results obtained with carbamide are beyond doubt too low, and this method is not trustworthy, as proved by the following analysis of the sodium nitrite by Rupp's method (*loc. cit.*).

Expt. 11.—0.069 Gram of sodium nitrite was dissolved in 40 c.c. of  $N/10$ -potassium permanganate solution, to which a few small crystals of sodium carbonate were added. The solution was warmed on the water-bath for fifteen minutes, cooled, acidified with dilute sulphuric acid, and excess of potassium iodide then added; the liberated iodine was titrated with  $N/10$ -sodium thiosulphate.

20.7 c.c.  $N/10$ - $Na_2S_2O_3 \cdot 5H_2O$  required. Hence  $40 - 20.7 = 19.3$  c.c.  $N/10$ - $K_2MnO_8$  required for oxidation of the nitrite.  
(1 c.c. = 0.00345  $NaNO_2$ ) = 96.5 per cent.  $NaNO_2$ .

Another experiment gave as a result 97 per cent.  $NaNO_2$ , thus confirming the accuracy of the experiments with thiocarbamide.

*Analyses of Ethyl Nitrite in Alcoholic Solution.*

A dilute solution of ethyl nitrite was prepared according to the method described in the British Pharmacopœia, which yields a product containing as nearly as possible 3.5 per cent. of the pure ester. One c.c. of this solution should give, when analysed by the well-known method using potassium iodide, 7 c.c. of gas ( $NO$ ) at  $15.5^\circ$  and 760 mm.

Results using thiocarbamide, 1 c.c. of ethyl nitrite solution, 0.1 gram of thiocarbamide, dissolved in 1 c.c. of water, 1 c.c. of dilute acetic acid:

	Gas evolved.	Vol. (c.c.) at $15.5^\circ$ and 760 mm.
Expt. 12.	6.9 c.c. at $11.7^\circ$ and 758 mm. ....	6.88
Expt. 13.	6.9 c.c. at $12.1^\circ$ and 758 mm. ....	6.87

Estimated by the potassium iodide method, 1 c.c. of 10 per cent. potassium iodide solution, 1 c.c. of dilute sulphuric acid:

Expt. 14. 7 c.c. at 11.2° and 753 mm. .... 6.99

In order to obtain a further comparison of the two methods, a specimen of "sweet spirits of nitre" several months old was analysed, with the following results (2 c.c. of the sample were taken in each experiment):

#### A.—Thiocarbamide Method.

	Gas evolved.	Vol at N.T.P. in c.c.
Expt. 15.	4.6 c.c. at 14.6° and 751 mm. ....	4.24
Expt. 16.	4.5 c.c. at 14.6° and 751 mm. ....	4.15

#### B.—Potassium Iodide Method.

Expt. 17.	4.9 c.c. at 14.6° and 771.7 mm. ....	4.65
Expt. 18.	4.9 c.c. at 14.7° and 760.85 mm. ....	4.59

The greater divergence in the results by the two methods with the old specimen of the nitrite solution suggests that the accuracy of the potassium iodide method is probably affected by the presence of some ethyl nitrate in the sample, and the following results of the analysis of sodium nitrite in presence of some sodium nitrate appear to confirm this view.

0.069 Gram of sodium nitrite and 0.138 gram of sodium nitrate (that is, double the weight of the nitrite) were dissolved in 2 c.c. of water; 2 c.c. of potassium iodide solution were added, and having been introduced into the nitrometer, 2 c.c. of dilute sulphuric acid were added:

	Gas evolved.	Vol. at N.T.P. in c.c.	NaNO <sub>2</sub> per cent.
Expt. 19.	23.3 c.c. at 15.3° and 765.35 mm. ....	21.84	97.6
Expt. 20.	23.4 c.c. at 16.2° and 762.3 mm. ....	21.78	97.4

The mean result of these two determinations, namely, 97.5, is thus 0.74 per cent. higher than that obtained for the same specimen of sodium nitrite when analysed by the aid of thiocarbamide (see after Expt. 10), or by Rupp's method (*loc. cit.*). An alcoholic solution of commercial pure amyl nitrite was also found to give a somewhat higher result when analysed by means of potassium iodide, as compared with the thiocarbamide method.

#### *Analyses of the Gases Evolved when Nitrous Acid and Thiocarbamide interact in the presence of Acids of Different Strength and Constitution.*

In all the following experiments a milli-molecular proportion of thiocarbamide (0.076) and two milli-molecular proportions of the

acid were dissolved in about 2 c.c. of water and introduced into the nitrometer; 0.072 gram of sodium nitrite (equivalent to 0.069 of the pure salt) dissolved in 1 c.c. of water was then added.

After the evolution of gas had ceased, the volume was read off, and the nitric oxide was then absorbed by means of a fresh saturated solution of ferrous sulphate; the residual nitrogen was measured after complete absorption of the nitric oxide was ensured. Since the object in these experiments was merely to determine the relative proportions of the two gases evolved, the volume results obtained, corrected to the normal temperature and pressure, are alone given. The theoretical volume of the mixed gases is 22.36 c.c.:

EXPTS. 21-26.	Vol. at N.T.P. in c.c.	Vol. of NO.	Vol. of nitrogen.
Hydrochloric acid .....	22.37	21.47	0.9
Oxalic acid .....	22.41	19.87	2.54
Malonic acid .....	21.36	11.08	10.28
Succinic acid .....	22.16	4.29	17.87
Malic acid .....	22.25	3.83	18.42
Tartaric acid .....	22.36	12.37	9.99
Acetic acid .....	22.39	2.88	19.51
Propionic acid .....	22.42	2.60	19.82
Glycolic acid .....	22.49	7.30	15.19
Lactic acid .....	22.39	8.04	14.35
<i>o</i> -Nitrobenzoic acid .....	21.21	5.51	15.70
<i>m</i> -Nitrobenzoic acid .....	22.04	2.75	19.29
<i>p</i> -Nitrobenzoic acid .....	18.12	0.80	17.32
<i>o</i> -Bromobenzoic acid .....	21.06	6.69	14.37
<i>m</i> -Bromobenzoic acid .....	20.08	3.69	16.39
<i>p</i> -Bromobenzoic acid .....	22.63	0.00	22.63

In the experiments with the derivatives of benzoic acid, 2 c.c. of alcohol were used as solvent for the *o*- and *m*-compounds, and 4 c.c. for the *p*-compounds, on account of the sparing solubility of these acids in water; even then the reactions were not quite completed. The evolution of gas was very slow; twenty-four hours were required in the case of *p*-bromobenzoic acid. The results, however, show sufficiently the effects of these acids on the direction of the change.

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### CXXIX.—*Sylvestrene. The Constitution of d-Sylvestrene and its Derivatives.*

By WALTER NORMAN HAWORTH, WILLIAM HENRY PERKIN, JR.,  
and OTTO WALLACH.

DURING his researches on Swedish oil of turpentine, Atterberg (*Ber.*, 1877, 10, 1202; 1878, 11, 1698) made the important

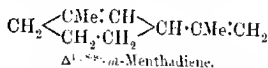
discovery that this oil contains, besides pinene, a new terpene which boils at 173–175°, and to which he gave the name *sylvestrene*. He showed that this terpene combines with two molecules of hydrogen chloride to yield sylvestrene dihydrochloride,  $C_{10}H_{16} \cdot 2HCl$ , which melts at 72°, and is so characteristic that its formation is one of the best means of identifying sylvestrene. At a later date, Wallach (*Annalen*, 1885, **230**, 241; 1887, **239**, 24; 1888, **245**, 272) also investigated Swedish oil of turpentine, and was able to confirm Atterberg's results in every particular; he also prepared the dihydrobromide,  $C_{10}H_{16} \cdot 2HBr$  (m. p. 72°), the dihydriodide,  $C_{10}H_{16} \cdot 2HI$  (m. p. 66–67°), the tetrabromide,  $C_{10}H_{16}Br_4$  (m. p. 135–136°), and the nitrosochloride,  $C_{10}H_{16}NOCl$  (m. p. 106–107°). By the decomposition of the pure dihydrochloride by means of potassium hydroxide or aniline, Wallach obtained an oil which did not boil constantly, and from which, by repeated fractionation, he isolated a specimen of sylvestrene, which had the following properties:

B. p. 175–176°;  $d_{20}$  0.848°;  $n_D$  1.47573;  $\alpha_D$  +66.32°,

and, as these properties were very similar to those of *d*-limonene, he suggested that sylvestrene probably belonged to the same group.

During the above fractionation the presence of a considerable quantity of a terpene of higher boiling point was observed, but this was at that time not further investigated.

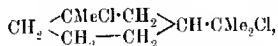
Subsequently Baeyer (*Ber.*, 1894, **27**, 3488, 3491; 1898, **31**, 1067, 1070) showed that sylvestrene is converted, by exhaustive bromination, into *m*-cymene, and that it therefore belongs to the group of the *m*-menthadienes; he expressed the opinion that carvostrene, which he had prepared from carone and which also belongs to the *m*-series, is the *dl*-modification of sylvestrene. Baeyer also suggested that the expression



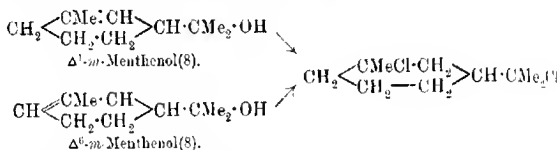
most probably represent both carvostrene and sylvestrene, but he did not bring forward any sufficient evidence that the double linking actually occupies the position assigned to it in this formula.

We have been engaged for some years on a series of experiments undertaken with the object of supplying a definite proof of the structure of sylvestrene, but the problem has proved to be a very difficult one. In the first place, Swedish oil of turpentine contains, besides sylvestrene, other terpenes boiling approximately at the same temperature, and it is therefore not possible to isolate sylvestrene from this oil by fractional distillation and directly to determine its properties. In order to obtain the sylvestrene, it is

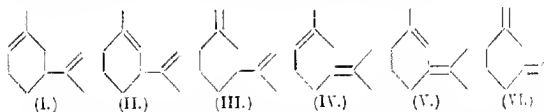
necessary to convert the fraction of the terpenes boiling at 173–178° into the dihydrochlorides, to isolate the characteristic sylvestrene dihydrochloride by recrystallisation, and then to decompose this by bases in the usual manner. It has long been assumed that this dihydrochloride has the constitution represented by the formula:



but the first proof of this was the observation that *dl*- $\Delta^1$ -*m*-menthenol(8) (Perkin and Tattersall, T., 1907, **91**, 481) and *dl*- $\Delta^6$ -*m*-menthenol(8) (Fisher and Perkin, T., 1908, **93**, 1888) both yield carvestrene dihydrochloride on treatment with hydrochloric acid:



and, further, that *d*- $\Delta^6$ -*m*-menthenol(8) is converted by hydrochloric acid into sylvestrene dihydrochloride, which is thus proved to be the *d*-constituent of carvestrene dihydrochloride (Perkin, P., 1910, **26**, 97).<sup>\*</sup> Although the constitution of sylvestrene dihydrochloride may now be considered as definitely established, this is not the case with sylvestrene itself, because it is obvious that the following terpenes might result from the elimination of two molecules of hydrogen chloride from sylvestrene dihydrochloride:



Of these, (IV), (V), and (VI) are out of the question, because they represent inactive configurations, whilst sylvestrene is active, and formula III, although it must be taken into account, is nevertheless highly improbable, because it does not account in a satisfactory manner for several of the properties of sylvestrene; it follows, therefore, that the two formulae which require the most careful consideration are I and II.

The principal difficulty in investigating this matter is the long and tedious preparation of sylvestrene dihydrochloride from Swedish oil of turpentine which can hardly be carried out on a sufficient scale in ordinary laboratory apparatus. Fortunately.

<sup>\*</sup> This matter will be discussed more fully in Part II of this investigation.

during the last few years, Messrs. Schimmel & Co. have undertaken the preparation of relatively large quantities of sylvestrene dihydrochloride, and have generously placed at our disposal a considerable amount of this valuable material. We take this opportunity of thanking Messrs. Schimmel for their generous assistance, without which the present investigation could hardly have been attempted. The main objects which we have had in view during this series of experiments have been similar to those pursued by Wallach in his investigation of the other terpene dihydrochlorides, namely, the preparation and investigation of the hydrocarbon mixture obtained by the elimination of hydrogen chloride from sylvestrene dihydrochloride and of the sylveterpineols and sylveterpins which result from the action of alkalis on this dihydrochloride.

*Sylvestrene from Sylvestrene Dihydrochloride.*

It has already been mentioned that Wallach had observed in 1885 that the substance obtained from sylvestrene dihydrochloride by the action of bases did not distil at a constant temperature, but he ultimately succeeded in isolating a fraction boiling at 175—176° which had  $\alpha_D +66.32^\circ$ . The subsequent development of the chemistry of the terpenes has made it clear that a single substance is not to be expected as the result of this elimination of hydrogen chloride, since, although the possibility of the formation of isomerides in the *p*-series is not so great as in the *m*-series, experiment has shown that the hydrocarbons formed by the removal of hydrogen chloride from dipentene and terpinene dihydrochlorides are always mixtures. We have now very carefully investigated this matter, and have submitted a large quantity of the mixture of terpenes resulting from the action of diethyl-aniline on pure sylvestrene dihydrochloride and subsequent distillation in steam, to very careful fractionation with a Young column. After the third fractionation, an oil was collected, which distilled at 174—176°, and has  $\alpha_D +66.05^\circ$ , but, as the fractionations were continued, the values for  $\alpha_D$  continually rose until at the tenth operation a hydrocarbon was obtained which distilled at 175°; 751 mm. and had the high value  $\alpha_D +83.18^\circ$  at 18°. The quantity had then become too small for further fractionation. The physical properties of this fraction were as follows:  $d_{15} 0.8479$ ;  $n_D 1.4760$ ;  $M 45.21$  (calc. for  $C_{10}H_{16}$ , 45.24), and, with the exception of the higher rotation, these values correspond closely with those previously found by Wallach for the fraction 175—176°, namely,  $t_D 0.848^\circ$ ;  $n_D 1.4757$ , and  $\alpha_D +66.32^\circ$ .

We next carefully examined a considerable quantity of the higher fractions which had accumulated, and, as the result of a

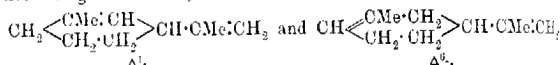


large number of fractionations, succeeded in isolating an oil which distilled at 182—184°/755 mm., and gave the following results on analysis:

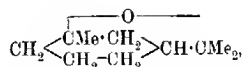
0.1587 gave 0.5716 CO<sub>2</sub> and 0.1692 H<sub>2</sub>O. C=87.9; H=11.8.

C<sub>10</sub>H<sub>16</sub> requires C=88.2; H=11.8 per cent.

The physical properties of this fraction were the following:  $d_{17}$  0.870;  $n_D$  1.4896; M 45.16; and  $\alpha_D$  +45.42°. It will be observed that the values for  $d$  and  $n_D$  are considerably higher than those of the fraction 175°, whereas  $\alpha_D$  is much lower. The oil distilling at 182—184° resinifies readily in contact with air, and also on distillation over sodium, and, when it is mixed with a saturated solution of hydrogen chloride in glacial acetic acid, it yields a large crop of crystals of sylvestrene dihydrochloride. It is probable that this fraction contains a considerable proportion of inactive sylvesterpinenolene (p. 1237) mixed with some isomeride of similar boiling point, but having a high rotation. There is reason to believe that the fraction of boiling point 175° and rotation +83.18° is still not a single substance, but is a mixture of the  $\Delta^1$ - and  $\Delta^6$ -isomerides



(compare p. 1230), and this point will be more fully discussed in Part II of this investigation. It may here be stated that several experiments were made in the endeavour to obtain a sylvestrene of definite constitution from sylvesterpine by the elimination of water under different conditions, but without success. The reason for the failure lies in the fact that this dihydroxy-derivative of sylvestrene exhibits a marked tendency to lose water with the formation of *m*-cineole:



which cannot be separated from the terpene, and even a small quantity of which has a marked influence on its physical properties. During the course of their experiments on the synthesis of carvestrene, Perkin and Tattersall (T., 1907, **91**, 485, 503) isolated *dl*-*m*-cineole from the products of the action of magnesium methyl iodide on ethyl cyclohexanone-3-carboxylate, and showed that it distilled at 177—178°, so that it would be impossible to separate a mixture of this substance and sylvestrene by fractional distillation.

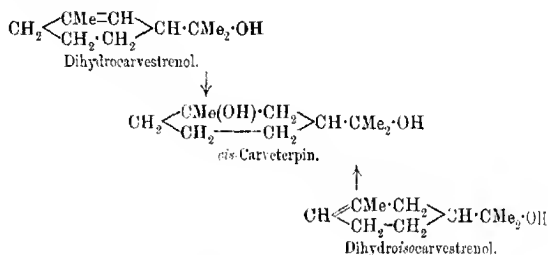


During the course of the earlier investigations on sylvestrene dihydrochloride (Wallach, *Annalen*, 1907, 357, 73), it was shown that an unsaturated alcohol (sylveterpineol, compare p. 1234) and a terpin (sylveterpin) are produced when the dihydrochloride is shaken with dilute aqueous potassium hydroxide. At that time, however, the terpin was isolated only as one modification melting at 136°. Further experiments have shown that besides this, a second modification is also produced during the action of dilute potassium hydroxide on sylvestrene dihydrochloride, which is much more soluble and melts at a lower temperature. In order to isolate this, the crude terpin obtained in the manner already described (*loc. cit.*), which melts roughly at 50–60° and distills at 144°/16 mm., is dissolved in benzene, and fractionally precipitated by light petroleum. During this process the  $\alpha$ -sylveterpin of higher melting point separates first, and this after recrystallisation melts at 137–138°, and is dextrorotatory, the solution in chloroform having  $\alpha_D + 27.74^\circ$ ; it sublimes readily, even on the steam-bath. The mother liquors contain the modification of lower melting point, and, on account of the sticky impurities which are present and very difficult to remove, the isolation of this  $\beta$ -sylveterpin in a pure condition is a very troublesome matter. After repeated fractional crystallisation it was found to melt at 70–75°, and have  $\alpha_D + 20.93^\circ$  (in chloroform) and  $+18.48^\circ$  in methyl alcohol. It was subsequently found that both modifications are produced when sylveterpineol is shaken with dilute sulphuric acid for several days. In this experiment sylveterpineol (compare p. 1234) (8 grams) was shaken on the machine with sulphuric acid (6 grams) and water (600 c.c.) for several days, the product neutralised with sodium carbonate, and, after the unchanged sylveterpineol had been removed by distillation in steam, the residue was several times extracted with chloroform. After the chloroform had been removed by evaporation, a syrupy mass was obtained, which, when rubbed with light petroleum, soon crystallised, and, after the substance had been left in contact with porous porcelain until quite dry, it was separated into the *cis*- and *trans*-( $\beta$ - and  $\alpha$ -)modifications of sylveterpin by fractional crystallisation in the manner just described.

It follows from these experiments that the sylvestrene derivatives yield *cis*- and *trans*-terpins under exactly the same conditions as the corresponding derivatives in the para-series.

The *cis*- and *trans*-modifications of sylveterpin are the *d*-constituents of the *cis*- and *trans*-carveterpins (tetrahydrocarvestrenediols),

the former of which (*cis*-) melts at 90°, and was first prepared by Perkin and Tattersall (T., 1907, **91**, 501) from dihydrocarvestrenol, and subsequently by Fisher and Perkin (T., 1908, **93**, 1889) from dihydroisocarvestrenol, in both cases by the action of dilute sulphuric acid:



*trans*-Carveterpin melts at 126—127°, and was first described by Baeyer (*Ber.*, 1894, **27**, 3490), who obtained it from carvestrene dihydrobromide by the action of silver acetate, and then of methylalcoholic potassium hydroxide. When *trans*-sylveterpin (6 grams) was digested in an apparatus provided with an efficient condenser, with permanganate (7.4 grams) dissolved in water (220 c.c.) for fifteen minutes, and the volatile products distilled off, the distillate gave the iodoform reaction, and, on treatment with phenylsemicarbazide, the phenylsemicarbazone of acetone was obtained, melting at 154—155°, showing that acetone is a product of the oxidation of *trans*-sylveterpin under these conditions.

*Sylveterpineol (Sylvestrol)*,  $\text{C}_{10}\text{H}_{17}\text{OH}$ .

This important derivative, which is obtained as the principal product, together with sylveterpin and about 5 per cent. of hydrocarbon, when sylvestrene dihydrochloride is shaken with dilute potassium hydroxide (compare Wallach, *Annalen*, 1907, **357**, 74) distils at 214°, and has  $d_4^{20}$  0.924;  $n_D^{20}$  1.4822 at 22°;  $M$  47.53 (calc. 47.96), and  $\alpha_D^{20}$  + 45.9°.

It was also shown that this unsaturated alcohol is oxidised by dilute permanganate, with formation of the corresponding glycerol,  $\text{C}_{10}\text{H}_{17}(\text{OH})_3$ , which was obtained as a viscid syrup, and distilled at 165°/11 mm. It has now been found that this syrup partly crystallises when it is rubbed with light petroleum and allowed to remain in a desiccator, and, after contact with porous porcelain, the solid residue was purified by recrystallisation from a mixture of acetic

ester and light petroleum. The sylveglycerol thus obtained melted at  $105^{\circ}$ , and gave the following results on analysis:

0.1170 gave 0.2740  $\text{CO}_2$  and 0.1130  $\text{H}_2\text{O}$ .  $\text{C} = 63.8$ ;  $\text{H} = 11.0$ .  
 $\text{C}_{10}\text{H}_{20}\text{O}_3$  requires  $\text{C} = 63.8$ ;  $\text{H} = 10.7$  per cent.

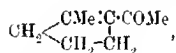
Since the original syrupy glycerol gave results on analysis (*loc. cit.*) which agreed closely with the formula  $\text{C}_{10}\text{H}_{20}\text{O}_3$ , it is clear that it consists of a mixture of isomeric glycerols, but the nature of these could not be determined. When the crude glycerol is warmed with dilute sulphuric acid, a ketone is formed which has the odour of menthone, and yields a semicarbazone melting at  $190$ – $192^{\circ}$ , and at the same time a hydrocarbon is produced which has the odour of cymene, distils at  $177^{\circ}$ , and doubtless consists of *m*-cymene.

During the oxidation of sylveterpineol with permanganate other substances besides the glycerol just described are produced, and as their nature seemed likely to afford evidence of the constitution of the terpineol these have been carefully investigated.

Sylveterpincol, in portions of 6 grams, was mixed with powdered ice and oxidised at  $0^{\circ}$  by the gradual addition of a solution of 8.2 grams of permanganate in 300 c.c. of water, the whole being well stirred during the operation. As soon as the oxidation, which takes about an hour, was complete, the filtrate from the manganese precipitate was saturated with carbon dioxide, distilled in steam (A), and the distillate mixed with ammonium sulphate and extracted with ether. After drying and evaporating, a small quantity of an oil was obtained, which had the odour similar to that of camphor and cyclohexanone, and distilled at  $185$ – $190^{\circ}$ :

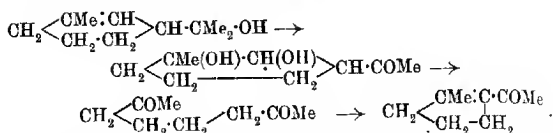
0.1002 gave 0.2836  $\text{CO}_2$  and 0.0917  $\text{H}_2\text{O}$ .  $\text{C} = 77.3$ ;  $\text{H} = 10.1$ .  
 $\text{C}_8\text{H}_{12}\text{O}$  requires  $\text{C} = 77.4$ ;  $\text{H} = 9.7$  per cent.

There can be little doubt that this ketone is 2-acetyl-1-methyl-4-cyclopentene,



because it yields a semicarbazone, which is sparingly soluble in alcohol, melts at  $220^{\circ}$ , and the mixture of which with the semicarbazone of acetylmethylcyclopentene (T., 1908, 93. 1916; Ber., 1909, 42. 146) melts at the same temperature.

This formation of acetylmethylcyclopentene is evidently due, in the first place, to the oxidation of sylveterpineol to diacetylbutane, which, as Marshall and Perkin (T., 1890, 57, 242) have shown, very readily undergoes internal condensation with the formation of methylidihydropentene methyl ketone (acetylmethylcyclopentene):

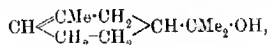


The alkaline residue from the steam distillation (A) was first extracted with ether in the Hagemann continuous extraction apparatus in order to remove neutral substances, then acidified with hydrochloric acid, and again extracted in the same apparatus. After drying, the ethereal solution was evaporated, and the yellow, syrupy residue heated at 100° for two hours in order to convert as much as possible of the ketohydroxy-acid, which was evidently present, into the corresponding lactone. The product was dissolved in ether, the ethereal solution extracted with sodium carbonate to remove any acid present, dried over potassium carbonate, evaporated, and the residue fractionated, when the greater portion distilled at 175°/25 mm., and gave the following analytical results:

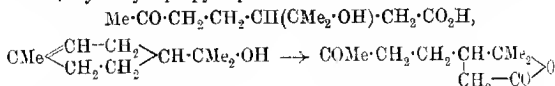
0.1077 gave 0.2570 CO<sub>2</sub> and 0.0874 H<sub>2</sub>O. C=65.1; H=9.0.

C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> requires C=65.2; H=8.7 per cent.

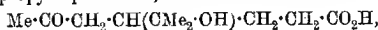
*Titration.*—0.1434 Gram was dissolved in excess of warm N/10-NaOH and titrated back with N/10-H<sub>2</sub>SO<sub>4</sub>, when it was found that 0.0316 gram NaOH was required for neutralisation, whereas this quantity of a keto-lactone should neutralise 0.0312 gram. The presence of the acetyl group in the lactone is indicated by the fact that it yields iodoform when its solution in sodium hydroxide is treated with iodine, and there can be little doubt that it is the product of the oxidation of Δ<sup>6</sup>-*m*-menthenol(8),



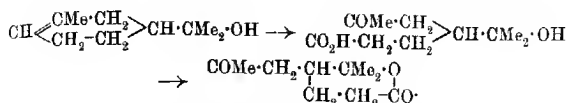
one of the constituents of sylveterpineol. Wallach (*Annalen*, 1893, **275**, 153) has shown that ordinary terpineol yields the γ-lactone of ε-keto-β-hydroxyisopropylheptonic acid,



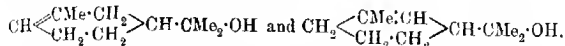
on oxidation with permanganate (compare also the formation of the lactone of α-methyl-γ-hydroxyisopropyladipic acid from Δ<sup>3</sup>-*m*-menthenol(8), T., 1910, **97**, 2132). In the present case the oxidation evidently proceeds with the formation of the δ-lactone of ε-keto-γ-hydroxyisopropylheptonic acid,



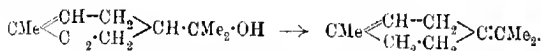
according to the scheme:



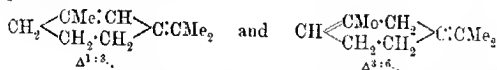
The formation of this  $\delta$ -ketolactone, on the one hand, and of 2-acetylmethylcyclopentene on the other, seems to us to prove conclusively that the sylveterpineol obtained by the action of dilute alkalis on sylvestrene dihydrochloride is a mixture of  $\Delta^8$ -*m*-menthenol(8) and  $\Delta^1$ -*m*-menthenol(8):



*Action of Oxalic Acid on Sylveterpineol.*—Wallach and Kerkhoff (*Annalen*, 1893, 275, 107) and Baeyer (*Ber.*, 1894, 27, 448) have shown that ordinary terpineol loses water with formation of terpinolene and some cineole when it is digested with aqueous oxalic acid:



With the object of studying the corresponding decomposition in the *m*-series, sylveterpineol was digested with 15 per cent. aqueous oxalic acid, the oily layer separated and fractionated, when a hydrocarbon was isolated, which distilled at 185° and was almost inactive. When this hydrocarbon was freshly distilled and at once analysed, it gave results somewhat too low for those required by the formula  $\text{C}_{10}\text{H}_{16}$ , due doubtless to the presence of *m*-cineole, and on keeping for a few hours it had absorbed oxygen and commenced to resinify. It is probable that this substance contains a mixture of the two *m*-terpinolenes:

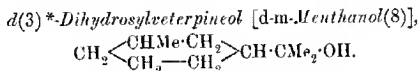


and evidence in support of this view was supplied by the observation that, when the mixture is treated with hydrogen chloride, it yields *dl*-sylvestrene dihydrochloride (carvestrene dihydrochloride), melting at 50–52°.

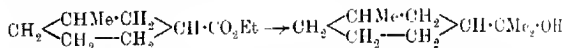
*Conversion of Sylveterpineol into m-Cymene.*—This change may be readily accomplished in the following manner: Sylveterpineol (10 grams), dissolved in glacial acetic acid (25 c.c.) and cooled at 0°, is gradually mixed with bromine (3.3 c.c.) and cautiously heated by a small flame.

In a short time evolution of hydrogen bromide commences, and is almost complete in about an hour; the product is, however, boiled for some hours, neutralised with alkali, and distilled in steam until

no more oil passes over. The distillate is mixed with ice, and shaken with permanganate until the colour remains; it is then again distilled, and the oil separated and distilled over sodium. In this way 5.8 grams of an oil were obtained, which boiled constantly at 175—176°, and, when oxidised with permanganate under the conditions recommended by Wallach (*Annalen*, 1893, **275**, 159), yielded *m*-hydroxyisopropylbenzoic acid, melting at 123—124°. The oil was therefore *m*-cymene.



During the course of a series of experiments on the reduction of alicyclic compounds (*Annalen*, 1911, **381**, 60) Wallach showed that sylveterpineol, on reduction at the ordinary temperature with hydrogen in the presence of colloidal palladium under the conditions recommended by Paal (compare *Ber.*, 1905, **38**, 1398), yields a dihydrosylveterpineol, which distils at 206—208°, gives a phenylurethane melting at 71—74°, and is presumably structurally identical with the *dl*-*m*-menthanol(8), which Perkin and Tattersall (*T.*, 1905, **87**, 1102) had previously obtained from ethyl hexahydro-*m*-toluate (ethyl 1-methylcyclohexane-3-carboxylate) by the action of magnesium methyl iodide:



and which distilled at 102°/20 mm. The dihydrosylveterpineol from sylveterpineol is, however, optically active, and has  $\alpha_D + 10.35^\circ$ , and the following analytical and synthetical experiments prove conclusively that it has the constitution assigned to it at the head of this section.

*Oxidation of d(3)-Dihydrosylveterpineol by Chromic Acid to Acetone and dl-1-Methylcyclohexan-3-one.*†—After several preliminary experiments, the conditions which were found to give the most satisfactory results were the following. The dihydrosylveterpineol (3 grams) was dissolved in glacial acetic acid (10 c.c.), heated on the water-bath, and then a solution of chromic acid (6 grams) in water (3 c.c.) added drop by drop, when a vigorous reaction set in, causing the liquid to boil without any further external heat, and the process was finished in about ten minutes. The product was diluted with water, neutralised with sodium carbonate, and distilled in steam.

\* The number in brackets indicates the position of the asymmetric carbon atom to which optical activity is due.

† We are much indebted to Dr. Walther Ost for valuable assistance during the course of these experiments.

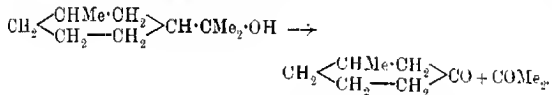
when an oil was obtained which yielded a crystalline semicarbazone (0.8—1 gram), and 15 grams of this derivative were prepared. On examination this proved to be unusually soluble in water and a mixture; the ketone was therefore regenerated and fractionated, the portion distilling at 170—172° being separately collected. This fraction contained an unsaturated substance, which was removed by permanganate, and the saturated ketone then yielded a semicarbazone, which, after crystallisation from a mixture of methyl alcohol and ether, melted at 186°:

0.1993 gave 0.4133 CO<sub>2</sub> and 0.1596 H<sub>2</sub>O. C=56.5; H=9.0.

C<sub>8</sub>H<sub>15</sub>ON<sub>3</sub> requires C=56.7; H=8.9.

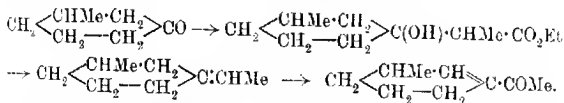
This inactive ketone has therefore the formula C<sub>7</sub>H<sub>12</sub>O, and proved to be 1-methylcyclohexan-3-one, since it yielded a sparingly soluble dibenzylidene derivative melting at 118°, and a phenylsemicarbazone melting at 186°. (Found, C=68.4; H=7.7. C<sub>14</sub>H<sub>19</sub>ON<sub>3</sub> requires C=68.5; H=7.8 per cent.)

Since during the oxidation of *d*(3)-dihydrosylvesterpineol, besides inactive 1-methylcyclohexan-3-one, acetone is also produced, and was identified by the iodoform reaction, it is clear that the decomposition can only be represented thus:



*Synthesis of d(1)-Dihydrosylvesterpineol.*

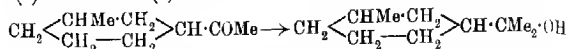
In carrying out this synthesis, *d*-1-methylcyclohexan-3-one (from pulegone) was converted by means of ethyl α-bromopropionate and zinc into 1-methyl-3-ethylidenecyclohexane by a process which has already been described (*Annalen*, 1908, 360, 51), and from this hydrocarbon the nitrosochloride and then the unsaturated ketone were prepared:



The *d*-3-methyl-Δ<sup>1</sup>-cyclohexenyl methyl ketone thus obtained is readily converted by reduction with hydrogen in the presence of colloidal palladium into 3-methylcyclohexenyl methyl ketone, which had already been prepared by Haworth and Wallach (*Annalen*, 1912, 389, 193) by the reduction of the nitrosochloride mentioned above. The physical properties of this ketone were not determined at that time; they have now been found to be as follows: B. p. 199—202°; *d*<sub>19</sub> 0.912°; *n*<sub>D</sub> 1.4517 at 19°; M 41.39 (calc., 41.61).



The pure ketone was now converted into *d*(1)-dihydrosylveterpineol *d*(1)-*m*-menthanol(8):



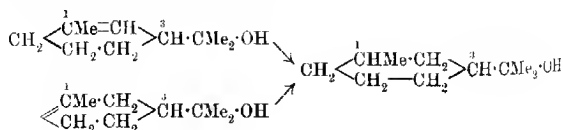
by the action of magnesium methyl iodide in the usual manner, and the tertiary alcohol thus obtained had not only the same odour as the specimen prepared by the reduction of *d*(3)-sylveterpineol (p. 1238), but also, with the exception of a somewhat lower rotation, the same physical constants:

0.1938 gave 0.5540 CO<sub>2</sub> and 0.2205 H<sub>2</sub>O. C=76.6; H=12.7.

C<sub>10</sub>H<sub>20</sub>O requires C=76.8; H=12.9 per cent.

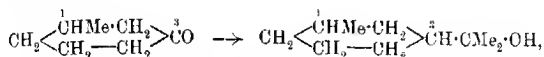
B. p. 206–209°; *d*<sub>20</sub> 0.9100°; *n*<sub>D</sub> 1.4663 at 20°; *α*<sub>D</sub> +1.96° (in methyl alcohol); M 175.0 (calc. 175.5). The two substances exhibit a slight difference in respect of the melting points of their phenylurethanes, since the phenylurethane of dihydrosylveterpineol from sylveterpineol melts at about 74°, whereas that of synthetical dihydrosylveterpineol, although it is in appearance and properties exactly similar to the substance of melting point 74°, melts at 82–83°. Before this difference could be explained it was important to prove that the two substances were actually structurally identical, and this was done by oxidation with chromic acid under the conditions given on p. 1238, when, like the dihydrosylveterpineol from sylveterpineol, the synthetical substance was converted into acetone and 1-methylcyclohexan-3-one, but with this difference, that, in the place of the inactive ketone obtained in the first case, the ketone resulting from the oxidation of synthetical dihydrosylveterpineol was the active modification, which has *α*<sub>D</sub> +8.8° and yields a phenylsemicarbazone melting at 169° and a dibenzylidene derivative melting at 127°. It seems at first sight remarkable that, whilst the strongly active dihydrosylveterpineol from sylveterpineol (*α*<sub>D</sub> +10.35°) yields, on oxidation, inactive 1-methylcyclohexan-3-one, the less active synthetical dihydrosylveterpineol (*α*<sub>D</sub> +1.96°) should, under the same conditions, yield the active ketone, but a careful consideration of the question suggests not only an explanation for this difference, but at the same time supplies further confirmation of the constitutional formulae proposed for sylveterpineol (p. 1237).

The two constituents of sylveterpineol contain one asymmetric carbon atom (3), which remains intact when this substance is reduced to dihydrosylveterpineol:



Carbon atom (1) in the two formulæ for sylveterpineol is not an asymmetric one, and when it becomes asymmetric by the reduction to *d*(3)-dihydrosylveterpineol, it can have no effect on the rotation of this terpineol, unless, indeed, asymmetric synthesis is assumed to take place. It follows, therefore, that the activity of *d*(3)-dihydrosylveterpineol from sylveterpineol is conditioned only by carbon atom (3), and, as the asymmetry of this is destroyed when this terpineol is oxidised to 1-methylcyclohexan-3-one, the inactive ketone should result, and this is actually the case.

In synthesising *d*(1)-dihydrosylveterpineol from *d*-1-methylcyclohexan-3-one:



the sign of the asymmetric carbon atom (1) in the ketone remains unchanged, but, on the other hand, carbon atom (3), although asymmetric, has been produced in equal quantities of *d*-(+) and *l*-(-).\*

It is clear that this modification of *d*-dihydrosylveterpineol must, on oxidation, give active *d*-methylcyclohexan-3-one, and this is again the case. It follows, therefore, that the two *d*-sylveterpineols—the one obtained from sylveterpineol by reduction and the other synthetically from *d*-methylcyclohexan-3-one—are isomeric substances, the isomerism being due to spatial differences in the nature of the asymmetrical carbon atoms (1) and (3). This explanation supplies an interesting and satisfactory reason for the slight differences observed in their optical and other properties, such as the melting points of the phenylurethanes.

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\* More strictly speaking, when sylveterpineol is reduced, the carbon atom (1) becomes an asymmetric one and, employing the usual formal conceptions of the spatial configurations of unsaturated compounds, it is evident that addition of hydrogen may occur at either side of the double linking, and consequently the distribution of atoms and groups about the carbon atom (1) may assume either the configuration *d*-(+) or *l*-(-). Judging by the difficulty experienced by chemists in establishing clear cases of asymmetric synthesis, the probabilities are considerably in favour of the production of equal numbers of molecules of each kind. If this were so, then any process which destroys the asymmetry of the carbon atom (3), will result in the production of a compound approximately one-half the molecules of which will contain carbon atom (1) in the *d*-(+) form, and the other half in the *l*-(-) form, and since this is the only asymmetric atom which remains, the product will be a nearly inactive mixture. Similar considerations apply to the second case.

CXXX. — *Cantharene and Other Hydrocarbons Allied to the Terpenes.*

By WALTER NORMAN HAWORTH.

THE dihydroxylenes, of which cantharene is perhaps the most interesting member, have several times within recent years claimed the attention of chemists, and yet as a class these hydrocarbons have never been completely investigated and definitely characterised.

Cantharene itself was first prepared by Piccard in the course of his classical researches on cantharidine. It is a dihydro-*o*-xylene,  $C_8H_{12}$ , as it yields *o*-toluic and phthalic acids on oxidation, and its isolation as a degradation product of cantharic acid afforded a valuable clue to the structure of cantharidine. Further interest attaches to this hydrocarbon because its close resemblance in properties to the terpenes led Piccard to regard it as the first artificially prepared terpene (*Ber.*, 1878, **11**, 2122; 1892, **25**, 2453).

Notwithstanding the interesting character of this substance it does not appear to have ever been prepared sufficiently pure for spectrochemical examination, the only optical constant available being the refractive index of the crude oil containing *o*-xylene as impurity ( $n_D = 1.49118$ ; Harries and Antoni, *Annalen*, 1903, **328**, 115).

Later, Baeyer synthesised a dihydro-*p*-xylene (*Ber.*, 1892, **25**, 2122), which he regarded as 1:4-dimethyl- $\Delta^{1:4}$ -cyclohexadiene, since it was prepared from ethyl succinylsuccinate by methylation and subsequent hydrolysis, reduction, and dehydration. Unfortunately the physical constants of this substance were not determined, and are thus not available for comparison.

Auwers has recently described another dihydro-*p*-xylene isomeric with the above, namely, 1:4-dimethyl- $\Delta^{1:3}$ -cyclohexadiene (*Ber.*, 1908, **41**, 1816), which he characterised by physical methods and by oxidation to acetylacetone.

A similar derivative of *m*-xylene figured for a long time in the literature as the product obtained by the elimination of water from methylheptenone by the use of various dehydrating reagents:

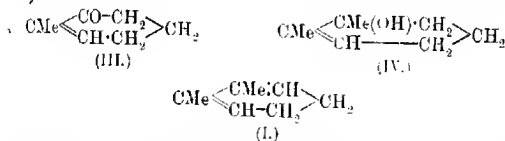


The hydrocarbon produced in this way has since been shown to consist principally of *m*-xylene and 1:3-dimethylcyclohexene, and to contain only little, if any, of the 1:3-dimethylcyclohexadiene (Wallach, *Annalen*, 1913, **395**, 74).

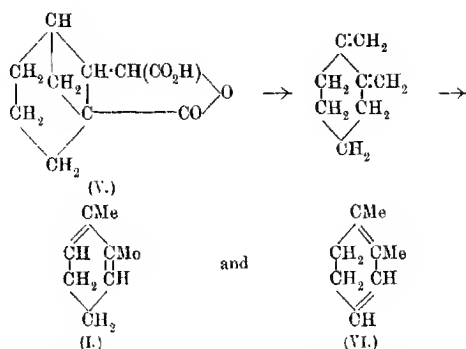
A dihydro-*m*-xylene is also mentioned by Harries and Antoni (*loc. cit.*), who prepared what they considered to be 1:3-dimethyl- $\Delta^{1,6}$ -cyclohexadiene by the dry distillation of the phosphate of 1,5-diamino-1:3-dimethylcyclohexane. The physical constants recorded for this hydrocarbon, however, seem clearly to indicate that it cannot have the arrangement of conjugated double linkings suggested by these authors, and the compound in all probability is 1:3-dimethyl- $\Delta^{1,4}$ -cyclohexadiene. The somewhat drastic treatment involved in the preparation of this substance has, indeed, been found in analogous cases to give rise to heterogeneous mixtures, and, owing to the wandering of substituent groups, the application of these conditions seems untrustworthy as a means of preparing a pure, homogeneous hydrocarbon (compare Crossley, T., 1909, 95, 930).

The close relationship which the dihydroxylenes bear to the members of the terpene group appeared to render them worthy of further investigation. With this object in view, a general method has been devised for the preparation of hydrocarbons of this character, the conditions employed being such as to lead to a homogeneous product of definitely known constitution.

When 1-methyl- $\Delta^6$ -cyclohexen-2-one (III) is treated with magnesium methyl iodide, the tertiary alcohol, 1:2-dimethyl- $\Delta^6$ -cyclohexen-2-ol or cantharene (IV) is formed, which is a viscid liquid distilling at 167°, and is the terpineol of the cantharene series. The dehydration of this substance leads to the corresponding hydrocarbon, 1:2-dimethyl- $\Delta^{2,6}$ -cyclohexadiene (I), distilling at 135.5° (corr.):

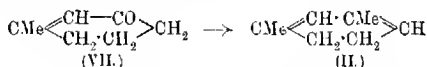


This dihydro-*o*-xylene seems to agree in all its properties with the hydrocarbon cantharene isolated by Piccard (*loc. cit.*); thus, it has a high refractive index which is comparable with the value found by Harries and Antoni (see p. 1242) for the hydrocarbon prepared from cantharidine, and it shows similar colour reactions and undergoes oxidation to *o*-toluic acid. The following scheme would seem to represent the change from cantharic acid (V) into cantharene, and although the latter substance would appear to consist principally of the compound I, yet it is extremely likely that there is some of the isomeric hydrocarbon (VI) also present:



It is unfortunate that the additive halogen compounds of cantharene are not crystalline substances, and consequently no direct comparison of the derivatives of the hydrocarbon prepared from natural and synthetic sources is possible.

The second example of the conversion of a ketone into a dihydroxylene was 1-methyl- $\Delta^1$ -cyclohexen-3-one (VII), which reacts similarly with magnesium methyl iodide, but the reaction, resulting in the former case in the isolation of an alcohol, could not be arrested at this intermediate stage, the product isolated on the present occasion being the hydrocarbon 1:3-dimethyl- $\Delta^1$ :3-cyclohexadiene, distilling at 135° (corr.):



This substance possesses properties analogous to the terpene group of hydrocarbons, and is characterised by its readiness in absorbing oxygen and resinifying, so that the preparation of pure specimens of both this and the former hydrocarbon was only achieved by careful fractionation over sodium in the absence of air.

The physical constants of the three dihydroxylenes, the constitutional formulae of which have been definitely established, are given below:

	(I.) $\Delta^1$ :5-Dihydro- o-xylene.	(II.) $\Delta^1$ :3-Dihydro- m-xylene.	Auwers' $\Delta^1$ :2,6- bisdio- <i>p</i> -xylene
B. p. ....	135.5°	135°	135—138°
D <sub>4</sub> <sup>20</sup> .....	0.8521	0.8373	0.830
n <sub>D</sub> <sup>20</sup> .....	1.4895	1.4856	1.4797
M .....	36.62	37.01	36.94

(N calculated, C<sub>8</sub>H<sub>12</sub> = 36.01.)

The chief point of interest in this comparison is the uniformly high values for molecular refraction,  $M$ , which show in every case optical exaltation. This phenomenon is explicable on the grounds that all these hydrocarbons possess a conjugated system of double bonds. Whilst the boiling point remains almost identical in each case, yet the density and refractivity values increase according as the substituent methyl groups approach one another, that is, in the order, para to ortho. The three hydrocarbons studied form therefore a series in which the only variant is the position of the methyl groups, so that the influence of the proximity of such substituent groups on the molecular refraction can be evaluated. It will be noticed that the exaltation is less evident in the ortho- than in the case of the para-, whilst the meta-compound exhibits a still greater exaltation than either (compare Auwers and Eisenlohr, *J. pr. Chem.*, 1911, [ii], 84, 37).

The physical constants recorded for the above hydrocarbons show a remarkably close parallelism with the values already found for the three xylenes themselves. The refractive indices tabulated below were determined by Sir W. H. Perkin (T., 1900, 77, 267), and the densities quoted are those recently given by Richards in his Faraday Lecture (T., 1911, 99, 1211):

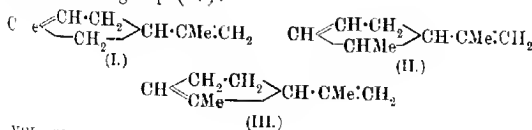
	<i>o</i> -Xylene.	<i>m</i> -Xylene.	<i>p</i> -Xylene.
B. p. ....	144°	139°	136·2°
$D_4^{20}$ .....	0·8811	0·8658	0·8611
$n_D^{20}$ .....	1·51136	1·50324	1·4991
$M$ .....	36·06	36·21	36·15

( $M$  calculated.  $C_8H_{10}$  [ $\pi$ ] = 35·54.)

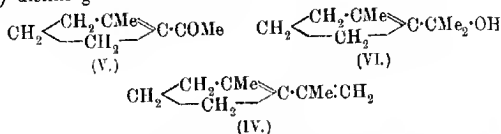
The same gradation in density and refractive power from the ortho- to the para-compound is noticeable, and there is a similar analogy between the two sets of values for molecular refraction.

This close comparison of the physical properties of the xylenes with their dihydro-derivatives lends support to the Kekulé formula representing these homologues of benzene, or preferably to Thiele's modification of this formula.

In this paper is also given an account of the synthesis of a new terpene of the cyclopentane series,  $C_9H_{14}$ . Some time ago Haworth and Perkin (T., 1908, 93, 573) published an investigation on the first known members of this series, consisting of three such hydrocarbons (I, II, III), and the present work contributes a fourth member of the group (IV):



The unsaturated ketone, 2-acetyl-1-methyl- $\Delta^1$ -cyclopentene (V) has been characterised for the first time, and its semicarbazone (m. p. 221°) prepared. This ketone reacts with magnesium methyl iodide with formation of the terpeneol (VI) of 1-methylisopropenyl-cyclopentene, which loses water and passes into the hydrocarbon (IV) distilling at 155–157°:



The physical and chemical properties of these substances are given in the experimental part. It will be observed that the boiling point of the hydrocarbon (IV) is higher than that of any of the previous members of the series, and this is doubtless attributable to the system of conjugated double linkings which the compound possesses, a factor which is also responsible for the exaltation in the value for molecular refraction (see p. 1250).

#### EXPERIMENTAL.

*Synthesis of 1:2-Dimethyl- $\Delta^{2:6}$ -cyclohexadiene ( $\Delta^{1:5}$ -dihydro-o-xylene),*  $\text{CMe} \begin{array}{c} \diagup \text{CMe} \cdot \text{CH} \\ \diagdown \text{CH} \cdot \text{CH}_2 \end{array} \text{CH}_2$ .

When the nitrosochloride of 1-methyl- $\Delta^1$ -cyclohexene\* is digested with anhydrous sodium acetate in glacial acetic acid, hydrogen chloride is eliminated with the formation of the oxime of 1-methyl- $\Delta^6$ -cyclohexen-2-one. This unsaturated ketone is easily regenerated from the oxime by the agency of dilute mineral acid in the presence of formaldehyde, and serves as the starting point of the present synthesis (compare Wallach, *Annalen*, 1908, **359**, 302).

1-Methyl- $\Delta^6$ -cyclohexen-2-one reacts vigorously with an excess of magnesium methyl iodide in dry ether. The product, after keeping for several hours, was decomposed with ice and water, distilled in a current of steam, and the distillate extracted with ether, dried, and distilled. A colourless oil, boiling at 167° under ordinary pressure, passed over, and this appeared to lose water during the

\* The following physical constants of 1-methylcyclohexan-1-ol (m. p. 24°) were determined:

$$d_4^{20} = 0.9302; n_D^{20} = 1.4620; M = 33.70. \quad (\text{Calc. } M = 33.85.)$$

On digesting 1-methylcyclohexan-1-ol with 10 per cent. aqueous oxalic acid for three hours and submitting the product to distillation in steam, the corresponding hydrocarbon was formed, namely, 1-methyl- $\Delta^1$ -cyclohexene, which, when rectified over sodium, distilled at 110–112°, and yielded a solid nitrosochloride melting at 95–97° (compare Wallach, *Annalen*, 1908, **359**, 287).

distillation. When the fractionation was carried out under diminished pressure, the pure carbinol, having the boiling point  $132^{\circ}/180$  mm., was obtained. This substance, 1:2-dimethyl- $\Delta^6$ -cyclohexen-2-ol or cantharenol, has a faint odour of menthol, and with concentrated sulphuric acid gives a deep orange-red coloration, whilst with acetic anhydride and a drop of concentrated sulphuric acid it yields an intense violet solution, changing rapidly into blue:

0.1270 gave 0.3540  $\text{CO}_2$  and 0.1260  $\text{H}_2\text{O}$ .  $\text{C}=76.0$ ;  $\text{H}=11.0$ .

$\text{C}_8\text{H}_{14}\text{O}$  requires  $\text{C}=76.2$ ;  $\text{H}=11.1$  per cent.

The physical constants of this alcohol were determined:

$D_4^{20}$  0.9528;  $n_D^{20}=1.4844$ ;  $M=37.86$  (Calc.,  $M=38.00$ ).

In contact with phenylcarbimide, dehydration of the carbinol took place instantaneously with formation of diphenylcarbimide, so that the urethane could not be prepared.

The whole of the 1:2-dimethyl- $\Delta^6$ -cyclohexen-2-ol was converted into the hydrocarbon, 1:2-dimethyl- $\Delta^{2,6}$ -cyclohexadiene, by digestion with 8 per cent. aqueous oxalic acid. The product was distilled in a current of steam, extracted with ether, dried over potassium carbonate, and rectified over metallic sodium in an atmosphere of hydrogen. A colourless oil having a strong odour of turpentine, and distilling constantly at  $135.5^{\circ}$  (corr.), was collected:

0.0987 gave 0.3210  $\text{CO}_2$  and 0.0972  $\text{H}_2\text{O}$ .  $\text{C}=88.7$ ;  $\text{H}=11.0$ .

$\text{C}_8\text{H}_{12}$  requires  $\text{C}=88.9$ ;  $\text{H}=11.1$  per cent.

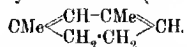
The hydrocarbon gave an orange-red coloration with concentrated sulphuric acid, and a carmine-red coloration, changing rapidly to reddish-brown, when to its solution in acetic anhydride a drop of concentrated sulphuric acid was added. It is further characterised by its extreme readiness in absorbing oxygen from the atmosphere and its tendency to polymerise to a hydrocarbon of higher boiling point; considerable difficulty was therefore encountered in the preparation of a specimen of such purity as to be available for analysis, and for the measurement of the physical constants of the substance:

$D_4^{20}$  0.8521;  $n_D^{20}=1.4895$ ;  $M=36.62$  (Calc.,  $M=36.01$ ).

The hydrocarbon was oxidised by digestion with dilute nitric acid ( $D 1.2$ ), and after evaporation of the mineral acid in a vacuum a solid residue was obtained which yielded a pure specimen of stearic acid, melting at  $103^{\circ}$ .



1:3-Dimethyl- $\Delta^{1:3}$ -cyclohexadiene ( $\Delta^{1:3}$ -Dihydro-m-xylene),



When 1-methyl- $\Delta^1$ -cyclohexen-3-one, prepared according to Knoevenagel's method (*Annalen*, 1894, **281**, 94), was submitted to the Grignard reaction under the conditions described in the previous case (p. 1246), and using magnesium methyl iodide as before, a pleasant smelling, light, volatile oil was obtained, which was sparingly soluble in water. This was extracted, and the major portion distilled between  $130^\circ$  and  $140^\circ$  under the ordinary pressure, leaving a slight residue which possessed a phenolic odour. On refractionation over metallic sodium in an atmosphere of hydrogen, the fraction of low boiling point distilled constantly at  $135\text{--}136^\circ$ :

0.0928 gave 0.3027  $\text{CO}_2$  and 0.0918  $\text{H}_2\text{O}$ . C=88.9; H=11.0.

$\text{C}_8\text{H}_{12}$  requires C=88.9; H=11.1 per cent.

An attempt was made to isolate the corresponding carbinol which would be the intermediate product formed in the above Grignard reaction. Dehydration seems, however, to be effected by contact with Grignard's reagent even in the cold, so that only the hydrocarbon could be isolated.

1:3-Dimethyl- $\Delta^{1:3}$ -cyclohexadiene is a colourless liquid, possessing a distinctive odour similar to that of pinene; it readily undergoes oxidation in the air, and resinifies. With concentrated sulphuric acid it gives an orange coloration, whilst acetic anhydride containing a drop of concentrated sulphuric acid produces a claret solution.

The following are the physical constants:

$d_4^{20}$  0.8373;  $n_D^{20}$  1.4856;  $M$ =37.01 (Calc.,  $M$ =36.01).

Klages (*Ber.*, 1907, **40**, 2362) mentions a substance identical in constitution with the above hydrocarbon, but the method of preparation, boiling point, and other important properties are not given.

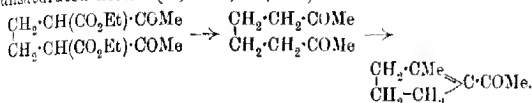
The *Dibromide*.—A solution of bromine in chloroform was slowly dropped into a well-cooled mixture containing 0.851 gram of the above hydrocarbon in 5 c.c. of chloroform, the bromine being readily absorbed. After 1.26 grams of bromine had been added, corresponding with one molecule, hydrogen bromide began to be evolved, although the solution remained only pale yellow on keeping. On the further addition of bromine the halogen continued to be absorbed with displacement of hydrogen, until in all 2.16 grams of bromine had been added, when the colour remained permanently red. Only liquid bromides could be isolated.

The *nitrosobromide* was prepared, and this also is a liquid.



and its Semicarbazone.

Marshall and Perkin first obtained this ketone by the hydrolysis of ethyl diacetyladipate with excess of methyl-alcoholic potassium hydroxide, diacetylbutane being an intermediate product which, under the conditions essential for the hydrolysis, undergoes internal condensation with loss of water and formation of the above unsaturated ketone (T., 1890, 57, 242):



The author has found the following to be the best method for the preparation of this ketone; crude ethyl diacetyladipate was digested for forty-eight hours with ten times its bulk of 10 per cent. aqueous sulphuric acid in a reflux apparatus, and then a brisk current of steam was passed through the liquid, when the unsaturated ketone was carried over. The steam distillate was saturated with ammonium sulphate, extracted twice with much ether, the extract dried over anhydrous magnesium sulphate, and the ether evaporated. The ketone distilled constantly at 189°, and the following physical constants were determined:

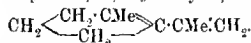
$D_4^{20}$  0.9542;  $n_D^{20}$  1.4869;  $M$  = 37.37 (Calc.,  $M$  = 36.49).

The *semicarbazone*, which has not previously been described, is a colourless, crystalline substance, melting at 221°, and is sparingly soluble in alcohol, from which it may be purified:

0.1086 gave 0.2372  $\text{CO}_2$  and 0.0812  $\text{H}_2\text{O}$ .  $C$  = 59.5;  $H$  = 8.3.

$\text{C}_6\text{H}_{12}\text{ON}_3$  requires  $C$  = 59.7;  $H$  = 8.3 per cent.

1-Methyl-2-isopropenyl- $\Delta^1$ -cyclopentene,



In order to prepare this hydrocarbon, a dry ethereal solution of diacetyl-1-methyl- $\Delta^1$ -cyclopentene (20 grams) was carefully added to a Grignard reagent consisting of 48 grams of methyl iodide and 8.2 grams of magnesium. A violent reaction ensued, and the product was kept overnight, then decomposed with ice, and the ether was removed by distillation in a current of steam. An oil possessing a pungent odour collected in the receiver, and this was extracted with ether, the product being fractionated under diminished pressure. The first fraction distilled at 85–95°/

45 mm., and a small proportion at 95—130°/45 mm. The first fraction was carefully redistilled over metallic sodium at the ordinary pressure in an atmosphere of hydrogen, when it was found to boil at 155—157°:

0.1431 gave 0.4627 CO<sub>2</sub> and 0.1426 H<sub>2</sub>O. C=88.2; H=11.1.

C<sub>9</sub>H<sub>14</sub> requires C=88.6; H=11.4 per cent.

The physical properties of this pure specimen were determined.

D<sub>4</sub><sup>20</sup> 0.8515; n<sub>D</sub><sup>20</sup>=1.4892; M=41.36 (Calc., M=40.63).

1-Methyl-2-isopropenyl-Δ<sup>1</sup>-cyclopentene is a terpene of the methyl-isopropylcyclopentane series (compare Haworth and Perkin, T., 93, 573); it possesses an odour similar to that of dipentene, and exhibits a tendency to polymerise to hydrocarbon which distil at a temperature intermediate between 157° and 175°. It is very unstable in contact with the air, from which it readily absorbs oxygen and resinifies. With acetic anhydride and a drop of concentrated sulphuric acid, it gives a deep crimson coloration exactly as do the members of the terpene group.

The second fraction, boiling at 95—130°/45 mm., was re-fractionated, when it was found to distil at 115°/30 mm., accompanied by the loss of a little water, and consequently good analytical results could not be obtained. There can be no doubt, however, that the substance distilling at the above temperature was the terpineol, 1-methyl-2-isopropenol-Δ<sup>1</sup>-cyclopentene, since the above hydrocarbon was obtained from it by the elimination of water. It possesses a pleasant odour resembling that of camphor.

The dibromide.—0.892 Gram of 1-methyl-2-isopropenyl-Δ<sup>1</sup>-cyclopentene was dissolved in 5 c.c. of chloroform, and the solution cooled to -10°. A solution of bromine in chloroform was gradually added from a burette, and after the first few drops the product assumed a deep red colour, although bromine continued to be absorbed. When 1.164 grams of bromine had been added, hydrogen bromide began to be evolved in copious clouds on each subsequent addition of the bromine solution. The end point of absorption was thus easy of detection. This amount of bromine is equivalent to one molecule, 1.17 grams being the theoretical amount required for the weight of hydrocarbon taken. The solution, which had acquired a deep permanganate coloration, was allowed to evaporate in the air, when a heavy oil remained, which did not crystallise.

The author is indebted to the Chemical Society for a grant, which has defrayed the expenses of this investigation.

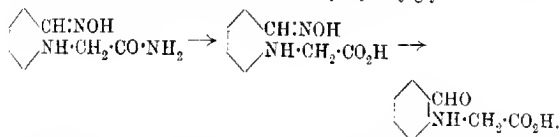
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,  
UNIVERSITY OF ST. ANDREWS.

CCXXXI.—*The Synthesis of o-Aldehydophenyglycine.*

By WILHELM GLUUD.

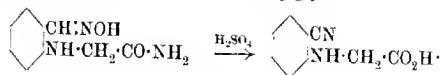
IN spite of the importance of phenylglycine-*o*-carboxylic acid in technical chemistry, the corresponding *o*-aldehydophenyglycine does not seem to have been prepared. The synthesis of this compound was a matter of considerable interest, as it seemed likely it might be an excellent source for the preparation of indole and its derivatives.

The direct interaction of *o*-aminobenzaldehyde and chloroacetic acid or its ester did not give good results, still less if the oxime was used instead of the aldehyde. A much better method was found in the decomposition of the oxime with chloroacetamide in the presence of calcium carbonate. The oxime of *o*-aldehydophenyglycineamide thus obtained, on boiling with alkali, gave the oxime of *o*-aldehydophenyglycine. By careful treatment of the oxime of *o*-aldehydophenyglycineamide with dilute sulphuric acid, the oximogroup also was eliminated, and *o*-aldehydophenyglycine obtained.



The *o*-aminobenzaldoxime required was prepared from *o*-nitrobenzaldehyde by reducing the oxime with ammonium sulphide according to the method given by Gabriel and Meyer (*Ber.*, 1881, 14, 2339; compare also Gabriel, *Ber.*, 1903, 36, 803).

When the oxime of *o*-aldehydophenyglycineamide was treated with concentrated sulphuric acid, a good yield was obtained of a crystalline compound, which, from its melting point and other properties, I believe to be *o*-cyanophenyglycine:

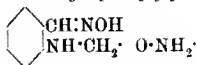


When the amide or the corresponding oxime of *o*-aldehydophenyglycine was fused with potassium hydroxide, phenylglycine-carboxylic acid and indigotin were obtained in quantities varying with the experimental conditions. The formation of indigotin was ascribed to the intermediate production of *o*-cyanophenyglycine. On dry distillation with lime, both the amide-aldoxime and the aldehyde gave indole or its derivatives. This reaction and other

experiments with *o*-aldehydophenylglycine will be further investigated.

#### EXPERIMENTAL.

*Oxime of o-Aldehydophenylglycineamide,*



*o*-Aminobenzaldoxime (22.5 grams) was heated with 17 grams of chloroacetamide, 9 grams of calcium carbonate, and 350 c.c. of water for three hours under a reflux condenser. The mixture was allowed to cool, and the crystalline powder formed was collected, treated with a small quantity of cold concentrated hydrochloric acid, and again collected, washed, and dried on a water-bath. The yield was 25.5 grams, or 80 per cent. of the theoretical. This compound was pure enough for most purposes, but for analysis 1 gram was redissolved in 200 c.c. of boiling water, from which the *oxime* crystallised in small, microscopic, colourless prisms or octahedra, melting and decomposing at 212–214:

0.1549 gave 0.3186  $\text{CO}_2$  and 0.0808  $\text{H}_2\text{O}$ .  $\text{C}=56.10$ ;  $\text{H}=5.84$ .

0.1437 „, 26 c.c.  $\text{N}_2$  at  $15^\circ$  and 764 mm.  $\text{N}=21.33$ .

$\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$  requires  $\text{C}=55.93$ ;  $\text{H}=5.74$ ;  $\text{N}=21.76$  per cent.

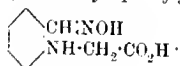
The *oxime* is scarcely soluble in cold water, and very sparingly so in organic media; when warmed with alkali it gives off ammonia. When heated with lime, considerable quantities of oily distillates are obtained, which give a marked reaction with pine-shavings, the odour of indole being at the same time observed.

The *oxime* was fused with potassium hydroxide, the reaction being carried out as follows. 7.5 Grams of potassium hydroxide and 2 c.c. of water were heated to  $170^\circ$ , and 0.6 gram of the *oxime* added to the fused mass. When it was well mixed, it was left in a closed vessel, with a stream of hydrogen passing through it, for two hours at  $210\text{--}220^\circ$ . The fused mass was treated with water, and the mixture, which had a dark colour owing to the formation of indigotin, was extracted with ether. The colouring-matter collected at the top, so that the aqueous lower layer could be separated. The latter was acidified with concentrated hydrochloric acid, and then extracted three times with ether, the ethereal solution evaporated, and the residue crystallised from water. In this way 0.2 gram of phenylglycine-*o*-carboxylic acid was obtained. Any rise in temperature was found to produce a corresponding increase in the yield of indigotin.

*o*-Cyanophenylglycine.

The oxime described above (0.5 gram) was warmed with 5 c.c. of concentrated sulphuric acid until it was dissolved. The solution was then poured on ice, when microscopic needles soon separated, which were collected, washed, and dried on a water-bath (0.4 gram). The compound melted and decomposed at about 192° after a previous short sintering.

It is scarcely soluble in alcohol or other organic solvents, but readily so in warm water, from which it does not crystallise. The substance is in all probability *o*-cyanophenylglycine, identical with that prepared according to the method described in D.R.P. 206903 (*Chem. Zentr.*, 1909, i, 807). Analysis gave nearly theoretical figures, but this cannot be entirely depended on, as the substance could not be purified by recrystallisation.

*Oxime of o*-Aldehydophenylglycine,

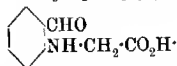
In order to prepare this compound, 10 grams of the oxime of *o*-aldehydophenylglycineamide were boiled with 125 c.c. of 2*N*-sodium hydroxide until all odour of ammonia had disappeared. The mixture was then cooled and treated with 250 c.c. of *N*-sulphuric acid. The crystals separating were collected and recrystallised from 125 c.c. of water. After drying on a water-bath, the yield of the *oxime of o*-aldehydophenylglycine was 8.2 grams, or 82 per cent. of the theoretical. The compound forms compact, spicular crystals, which melt and evolve gas at 134°. They are exceedingly soluble in ether, acetone, or alcohol, and fairly so in hot water or chloroform. For analysis, the compound was again recrystallised from water, then dissolved in methyl alcohol, and precipitated with water.

The product was almost pure white, with a yellow tinge. It was dried for an hour over phosphoric acid at 100°/10–12 mm., and then analysed:

0.2139 gave 0.1013 H<sub>2</sub>O and 0.4386 CO<sub>2</sub>. C=55.92; H=5.30.

0.1193 „ 14.8 c.c. N<sub>2</sub> at 20° and 758 mm. N=14.21.

C<sub>9</sub>H<sub>7</sub>O<sub>3</sub>N<sub>2</sub> requires C=55.64; H=5.19; N=14.44 per cent.

*o*-Aldehydophenylglycine,

The oxime of *o*-aldehydophenylglycineamide (3 grams) was boiled with 150 c.c. of 5*N*-sulphuric acid under a reflux condenser for ten minutes, then cooled, and the solution extracted twice with about 50 c.c. of ether. The ether was evaporated, and the residue dissolved in 50 c.c. of boiling xylene. On cooling, *o*-aldehydophenylglycine crystallised in aggregates of compact plates or tablets (1 gram). It is readily soluble in warm water, ethyl alcohol, or amyl alcohol, but sparingly so in benzene or chloroform.

On heating alone, or better with lime, a strong odour of indole is observed, and the vapours give a marked reaction with pine shavings.

If the hot aqueous solution is mixed with a solution of phenylhydrazine in glacial acetic acid, a voluminous precipitate is formed, consisting of fine, microscopic needles, which are only very sparingly soluble in hot water. The aldehyde also shows distinctly the colour reaction with acid magenta.

The aldehyde was purified by recrystallisation, first from methyl alcohol, and afterwards from a mixture of equal parts of water and methyl alcohol. The product, after drying in a desiccator over phosphoric acid, is colourless and without odour, and melts at 176–177° to a red liquid, from which a slow evolution of gas takes place:

0.2919 gave 0.6458 CO<sub>2</sub> and 0.1358 H<sub>2</sub>O. C=60.34; H=5.21.

0.1086 „ 7.5 c.c. N<sub>2</sub> at 18° and 758 mm. N=7.98.

C<sub>9</sub>H<sub>9</sub>O<sub>3</sub>N requires C=60.31; H=5.06; N=7.82 per cent.

When fused with potassium hydroxide, the aldehyde yields either phenylglycine-*o*-carboxylic acid or indigotin, according to the conditions. The calcium salt of *o*-aldehydophenylglycine is easily obtained by dissolving the aldehyde in *N*-sodium hydroxide and adding calcium chloride solution, when the calcium salt crystallises out. It seems to be a very suitable material for the preparation of indole or its derivatives.

DAVY FARADAY LABORATORY.

### CLXXXII.—*The Purification of Acetone by means of Sodium Iodide.*

By KATHLEEN SHIPSEY and EMIL ALPHONSE WERNER.

IN a recent note (P., 1913, 29, 117) it was shown that sodium iodide is capable of uniting with acetone to form a well defined crystalline compound having the composition  $\text{NaI} \cdot 3\text{C}_3\text{H}_6\text{O}$ , which easily gives off all the acetone on gentle warming. The compound may be readily prepared by dissolving anhydrous sodium iodide to the point of saturation in hot acetone and allowing the solution to cool to the ordinary temperature; if the liquid is cooled to about  $-8^\circ$  by means of ice and salt, the yield of crystals is largely increased.

Experiments have been made with the object of testing if the production of the above compound could be used for the preparation of pure acetone from the commercial material; the results, as seen below, are very satisfactory. A sample of ordinary dry acetone (about 500 c.c.) was distilled from a round-bottomed flask, provided with a three-section Young's evaporator still-head, and gave the following results: (a) b. p. corrected to 760 mm. =  $55.9-56.3^\circ$ ; (b)  $D_4^{20} = 0.8152$ ; (c) a few c.c. when added to a dilute solution of potassium permanganate caused immediate reduction of the latter. A quantity of the compound  $\text{NaI} \cdot 3\text{C}_3\text{H}_6\text{O}$  was prepared by dissolving 100 grams of anhydrous sodium iodide in the fresh distillate by heating gently on the water-bath; the crystals which separated on cooling were drained off so far as possible from the mother liquor, and quickly transferred to a dry flask, attached to a suitable condenser and receiver, and the acetone rapidly distilled off by gentle heat. The distillate after remaining for twenty-four hours over anhydrous calcium chloride was redistilled, using an evaporator still-head as before; the following results were obtained: (a) b. p. at 760 mm.  $56.1-56.2^\circ$ ; (b)  $D_4^{20} = 0.8130$ ; (c) a few c.c. added to solution of potassium permanganate produced no change even after standing for fifteen minutes.

A specimen of pure acetone from "bisulphite" (Kahlbaum) dried over calcium chloride gave (a) b. p. at 760 mm.  $56.1-56.2^\circ$ ; (b)  $D_4^{20} = 0.8138$ ; (c) no reducing action on potassium permanganate.

Timmermans, in the course of a careful investigation, "*Recherches expérimentales sur la densité des liquides en dessous de  $0^\circ$* " (*Sci. Proc. Roy. Dubl. Soc.*, 1912, 13, 330), has determined the boiling points and densities of specimens of acetone from bisulphite, purified by redistillation from several different dehydrating agents; the



purest product obtained by distillation from phosphoric oxide gave the values: (a) b. p. =  $56.10^{\circ} \pm 1$ ; (b)  $D_4^{20} = 0.81249 \pm 3$ , whilst a specimen from bisulphite (Kahlbaum) redistilled from calcium chloride gave this investigator the constants: b. p.  $56.1^{\circ}$  and  $D_4^{20} = 0.8137$ , a result almost identical with that found by us for a specimen purified in a similar manner. It is thus seen from the results just recorded that it is possible by means of sodium iodide to obtain pure acetone from the commercial article in a very simple manner, and whilst the product is quite equal in purity to that obtainable by the rather laborious bisulphite method, it is obvious that the process has the great advantage of being workable in a continuous manner, since the sodium iodide obtained after distilling off the acetone from the crystalline compound can be used repeatedly for obtaining a further supply of the compound either from the mother liquor or from a fresh quantity of ordinary acetone. In connexion with this point it was noticed that the sodium iodide left after distillation of the acetone from the crystals  $\text{NaI} \cdot 3\text{C}_2\text{H}_5\text{O}$  was much more readily soluble in fresh acetone than the original salt used; this was found to be due to the abstraction of a certain amount of water from the acetone by the anhydrous salt, with formation of some of the dihydrate. The latter salt may be easily dissolved in its own weight of acetone at the ordinary temperature, and the resulting solution when cooled to about  $-8^{\circ}$  yields a considerable quantity of the acetone compound, for this reason: the hydrated sodium iodide can be used with advantage for the preparation of a quantity of pure acetone when there is no desire to go beyond the trouble of a single operation.

The following results represent the wide difference in the proportions of pure acetone obtained in a single operation, using the different specimens of sodium iodide:

	Calculated on weight of crude acetone used.
I. Fresh anhydrous sodium iodide, yield.....	26.8 per cent.
II. Sodium iodide left after distilling the acetone from the compound $\text{NaI} \cdot 3\text{C}_2\text{H}_5\text{O}$ .....	48.1 " "
III. $\text{NaI} \cdot 2\text{H}_2\text{O}$ .....	70.0 " "

So far as could be ascertained, the purity of the acetone was the same in each case. It may be mentioned in conclusion that whereas the compound  $\text{NaHSO}_3 \cdot \text{C}_2\text{H}_5\text{O}$  contains only 35.8 per cent. of acetone, the compound  $\text{NaI} \cdot 3\text{C}_2\text{H}_5\text{O}$  can yield without loss 53.7 per cent. of the ketone, and this yield is exceeded from the crystalline deposit obtained by cooling the acetone solution in a mixture of ice and common salt, indicating the formation of a compound containing a still larger proportion of acetone of crystallisation.

## EXPERIMENTAL.

The following experimental details explain the results recorded above:

I. One hundred grams of finely powdered anhydrous sodium iodide required for complete solution 440 grams of ordinary acetone at the boiling point.

The solution was cooled in a mixture of ice and salt to  $-8^{\circ}$ .

Weight of crystals obtained = 198 grams.

Weight of pure acetone on distillation = 118 grams.

Weight of residual sodium iodide = 70 grams.

There was a loss of 10 grams of acetone; this is partly due to vaporisation from the crystals during the process of draining away the mother liquor.

II. One hundred grams of sodium iodide obtained from a previous distillation of the compound  $\text{NaI} \cdot 3\text{C}_2\text{H}_5\text{O}$  required for complete solution 270 grams of acetone at the boiling point. Solution cooled as before.

Weight of crystals obtained = 210 grams.

Weight of pure acetone on distillation = 130 grams.

Weight of residual sodium iodide = 78 grams.

III. One hundred grams of  $\text{NaI} \cdot 2\text{H}_2\text{O}$  taken, dissolved in 100 grams of acetone at the ordinary temperature. Cooled as before.

Weight of crystals obtained = 138 grams.

Weight of pure acetone on distillation = 70 grams.

Weight of residual sodium iodide = 62 grams.

The theoretical yield of acetone from 138 grams of the compound  $\text{NaI} \cdot 3\text{C}_2\text{H}_5\text{O}$  is 74.1 grams; the result which is in close agreement with this indicates that this compound only separates even at the low temperature when the hydrated sodium iodide is used; the presence of a relatively large proportion of water probably prevents the formation of a compound containing a larger proportion of acetone. It should be noted that the above proportions do not represent a saturated solution of sodium iodide dihydrate in the acetone, as in I and II; from a stronger solution it would not be possible easily to drain off the crystals so as to obtain pure acetone from the product.

UNIVERSITY CHEMICAL LABORATORY,  
TRINITY COLLEGE DUBLIN.

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CXXXIII.—*Colour and Constitution of Azomethine Compounds. Part III.*

By FRANK GEORGE POPE and WINIFRED ISABEL WILLETT.

ONE of the authors, in conjunction with R. Fleming (T., 1908, 93, 1918), pointed out that the salts of the azomethine compounds and their ethers exhibited an absorption totally different from that shown by the azomethines themselves, and suggested that the explanation of this fact was due to such substances existing as oxonium salts, whilst the azomethines possessed a normal configuration. A similar condition was also shown by Pope (*ibid.*, 533) to exist in the case of azomethine compounds containing a nitro- and a hydroxyl group in the para-position in each nucleus, the alkali salts showing an absorption markedly different from that exhibited by the azomethines, and the conclusion was drawn that in alkaline solution the compounds in question possessed a quinonoid configuration.

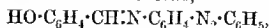
These results agree with Hewitt and Mitchell's observation (T. 1907, 91, 1251) that the lengthening of the chain of alternate double and single linkings accompanies the shifting of the absorption to the red end of the spectrum. In the hope of further confirmation of this fact, we have endeavoured to increase the length of the chain by preparing azomethine compounds from aminoazobenzene and *p*-nitroaminoazobenzene, but unfortunately in the latter case, although various methods of condensation have been tried, we have not been able to obtain any azomethines from the nitroaminoazobenzene.

Several azomethines prepared from aminoazobenzene have been obtained, and are described below, whilst one or two compounds related to *p*-nitroaminoazobenzene are also characterised.

EXPERIMENTAL.

Benzylideneaminoazobenzene has been obtained by Berju (*Ber.*, 1884, 17, 1403), who gives the melting point as 128°, but we find that the corrected value is 130.5° (Found, C=79.99; H=5.28; N=14.51. Calc., C=80.00; H=5.26; N=14.74 per cent.).

*p*-Hydroxybenzylideneaminoazobenzene,



was prepared by mixing equivalent quantities of its generators in hot alcoholic solution. The crystalline precipitate obtained is collected, washed, dried, and recrystallised from boiling toluene.

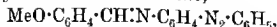
separating from the solvent in small, orange-yellow needles, which melt at  $231^{\circ}$  (uncorr.):

0.1436 gave 0.400  $\text{CO}_2$  and 0.0622  $\text{H}_2\text{O}$ .  $\text{C}=75.96$ ;  $\text{H}=5.13$ .

0.095 „ 10.4 c.c.  $\text{N}_2$  at  $21^{\circ}$  and 750 mm.  $\text{N}=14.02$ .

$\text{C}_{12}\text{H}_{15}\text{ON}_3$  requires  $\text{C}=75.75$ ;  $\text{H}=4.98$ ;  $\text{N}=13.95$  per cent.

*p*-Methoxybenzylideneaminoazobenzene,

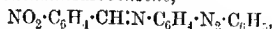


was obtained similarly from anisaldehyde and aminoazobenzene. It crystallises from glacial acetic acid in orange-brown plates, which melt at  $149^{\circ}$ :

0.1592 gave 0.4433  $\text{CO}_2$  and 0.0789  $\text{H}_2\text{O}$ .  $\text{C}=76.0$ ;  $\text{H}=5.51$ .

$\text{C}_{20}\text{H}_{17}\text{ON}_3$  requires  $\text{C}=76.19$ ;  $\text{H}=5.4$  per cent.

*p*-Nitrobenzylideneaminoazobenzene,

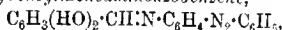


obtained similarly from *p*-nitrobenzaldehyde and aminoazobenzene, on recrystallisation from glacial acetic acid separates in small, orange plates, which melt at  $182.2^{\circ}$  (corr.):

0.1128 gave 0.2836  $\text{CO}_2$  and 0.0434  $\text{H}_2\text{O}$ .  $\text{C}=68.62$ ;  $\text{H}=4.27$ .

$\text{C}_{19}\text{H}_{14}\text{O}_2\text{N}_4$  requires  $\text{C}=69.09$ ;  $\text{H}=4.24$  per cent.

2:4-Dihydroxybenzylideneaminoazobenzene,



is obtained in the same manner from  $\beta$ -resorcyaldehyde and aminoazobenzene. It crystallises from alcohol in bronze leaflets, which melt and decompose at  $163^{\circ}$ :

0.1383 gave 0.3647  $\text{CO}_2$  and 0.0637  $\text{H}_2\text{O}$ .  $\text{C}=71.92$ ;  $\text{H}=5.12$ .

0.09 „ 10.4 c.c.  $\text{N}_2$  (dry) at  $19^{\circ}$  and 741.4 mm.  $\text{N}=13.17$ .

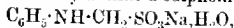
$\text{C}_{19}\text{H}_{15}\text{O}_2\text{N}_3$  requires  $\text{C}=71.94$ ;  $\text{H}=4.73$ ;  $\text{N}=13.25$  per cent.

With regard to the absorption spectra of the above compounds, the curves show a great similarity to that given by aminoazobenzene (Hewitt and Thomas, T., 1909, 95, 1295), the positions of the heads of the bands being as follows:

$\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$	about	1.5	2600
$\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_5$	„	1.5	2610
$\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$	„	1.5	2610
$\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$	„	1.5	2670
$\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$	„	1.5	2670

The *p*-nitroaminoazobenzene used was prepared by the method of the Aktien-Gesellschaft für Anilinfabrikation (D.R.-P. 131860), in which process diazotised *p*-nitroaniline is coupled with the sodium salt of monomethylaniline- $\omega$ -sulphonic acid, and the resulting compound decomposed with a warm dilute solution of sodium hydroxide.

The sodium salt of methylaniline- $\omega$ -sulphonic acid,



prepared by the condensation of aniline, formaldehyde, and sodium hydrogen sulphite, crystallises from dilute alcohol in small, colourless needles, which are very soluble in water:

0.1622 gave 9.7 c.c.  $N_2$  (dry) at  $16^\circ$  and 740 mm.  $N = 6.88$ .

0.3818 „ 0.1217  $Na_2SO_3$ ,  $Na = 10.32$ .

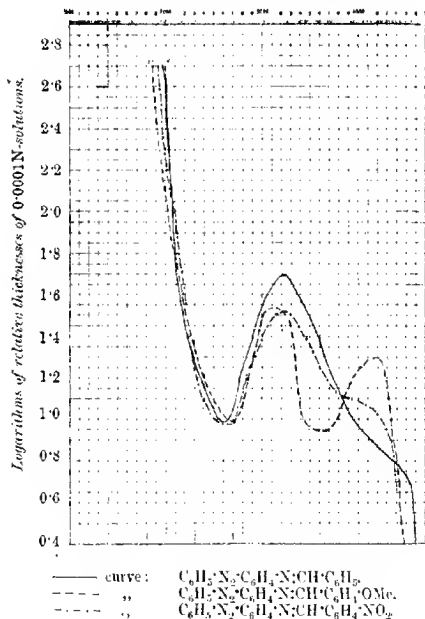
0.1705 lost 0.0139 at  $110^\circ$ .  $H_2O = 8.15$ .

$C_7H_8O_3NSNa \cdot H_2O$  requires  $N = 6.7$ ;  $Na = 10.13$ ;

$H_2O = 7.93$  per cent.

FIG. 1.

*Scale of oscillation frequencies.*



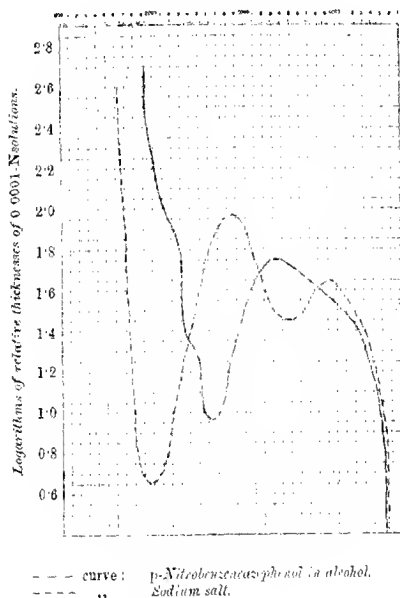
In coupling diazotised *p*-nitroaniline with the above sodium salt, a red precipitate of the salt  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot NO_2 \cdot Na$  is obtained, and may be purified by crystallisation from a mixture of equal volumes of alcohol and water, separating from the solvent in small, red needles:

0.1524 gave 20 c.c.  $N_2$  (dry) at  $17^\circ$  and 761 mm.  $N=15.47$ .

$C_{13}H_{11}O_3N_3SNa$  requires  $N=15.64$  per cent.

At the request of Dr. J. T. Hewitt we have prepared a specimen of *p*-nitrobenzeneazobenzeneazophenol by diazotising *p*-nitroaminoazobenzene and coupling with an alkaline solution of phenol. On mixing the diazo-solution with the alkaline phenol solution, a chocolate-coloured precipitate is obtained; this was collected,

FIG. 2.  
Scale of oscillation frequencies.



washed, and recrystallised from glacial acetic acid, in which solvent it is sparingly soluble. It melts at  $263^\circ$ , and dissolves in concentrated sulphuric acid with a characteristic violet colour:

0.1198 gave 0.2753  $CO_2$  and 0.0397  $H_2O$ .  $S=62.67$ ;  $H=3.68$ .

0.1116 " 0.253  $CO_2$  " 0.036  $H_2O$ .  $C=61.83$ ;  $H=3.58$ .

0.1074 " 19.6 c.c.  $N_2$  (dry) at  $21^\circ$  and 746 mm.  $N=20.78$ .

$C_{18}H_{13}O_3N_3$  requires  $C=62.24$ ;  $H=3.74$ ;  $N=20.18$  per cent.

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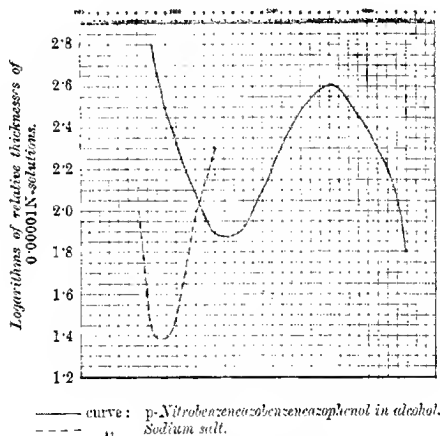
The hydrochloride, obtained by passing hydrogen chloride into a solution of the azophenol in xylene, is precipitated in small, violet needles.

The absorption curves of *p*-nitrobenzeneazophenol and *p*-nitrobenzeneazobenzeneazophenol and their sodium salts are shown in the annexed figures.

It will be noted that in the case of *p*-nitrobenzeneazophenol, the head of the band occurs at about  $1/\lambda$  2600, whilst on the addition of a little alkali, the head of the band is shifted to  $1/\lambda$  1950. With *p*-nitrobenzeneazobenzeneazophenol, the heads of the bands appear

FIG. 3.

Scale of oscillation frequencies.



at  $1/\lambda$  2550 and  $1/\lambda$  1830, a fact agreeing with Hewitt and Mitchell's observation (T., 1907, 91, 1251) that the longer the chain of alternate double and single linkings existing in the molecule, the less will be the chief oscillation frequency, and consequently the more blue the shade of the compound in question. This observation is strikingly confirmed in the case of the sodium salts of the two azo-compounds mentioned, for on dissolving them in dry xylene and adding an alcoholic solution of sodium ethoxide, *p*-nitrobenzeneazophenol gives a reddish-brown, crystalline precipitate of its sodium salt, whilst *p*-nitrobenzeneazobenzeneazophenol gives a purple, crystalline precipitate of the sodium salt.

In conclusion, we wish to tender our thanks to the Research Fund Committee of the East London College for a grant which has defrayed the cost of this investigation.

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#### CXXXIV.—*The Absorption Spectra of Some Thio-derivatives of Benzene.*

By JOHN JACOB FOX and FRANK GEORGE POPE.

PHENYL mercaptan differs from phenol in several important particulars. Some of the salts of phenyl mercaptan, such as the lead, copper, and silver salts, are coloured; and phenyl mercaptan does not readily combine with diazonium compounds to give thiolazo-derivatives (Hantzsch and Freese, *Ber.*, 1895, **28**, 3241), but yields instead thiophenyl ethers. As is well known, phenyl mercaptan undergoes oxidation with great readiness, forming diphenyl disulphide.

In view of these differences from phenol, we have examined the spectra of phenyl mercaptan and other thio-derivatives of benzene to ascertain in what way the characteristic spectrum of benzene was altered by the introduction of the thio-groups. A few observations of this character were made by Purvis, Jones and Tasker (*T.*, 1910, **97**, 2287).

The absorption spectrum of phenyl mercaptan exhibits no bands, but strong extensions of the spectrum occur in two places, one of which begins at about  $1/\lambda$  3600 (see diagram). This is in approximately the same position as the single persistent band of phenol (Hartley and Dobbie, *T.*, 1902, **81**, 930; Baly and Ewbank, *T.*, 1905, **15**, 1347). The addition of sodium ethoxide to a solution of phenyl mercaptan produces a profound change in the character of the spectrum. A band appears having its head at  $1/\lambda$  3730, and the whole spectrum is altered. The position of the bands in the case of sodium phenoxide and of sodium thiophenoxide is different, although in both the addition of sodium hydroxide has resulted in the displacement of the whole spectrum of the original substance towards the less refrangible region of the spectrum. This displacement of the spectrum appears to be a general effect of salt formation in phenols, and as regards the simpler phenols at all events the activity of the hydrogen atom of the hydroxyl or thiol group does



not appear to have much to do with the displacement of the region of absorption (compare Baly and Ewbank, *loc. cit.*). When the displacement of the band consequent on salt formation is sufficiently great, the region of absorption cuts into the visible spectrum, and coloured salts result.

The absorption spectrum of diphenyl disulphide,  $(C_6H_5)_2S_2$ , has no bands, and is unaltered by the addition of sodium ethoxide.

Since the spectra of phenol and phenyl mercaptan were found to be entirely different from one another, it became of interest to ascertain whether similar differences would be shown by related compounds, such as diphenyl ether,  $(C_6H_5)_2O$ , and diphenyl sulphide,  $(C_6H_5)_2S$ . The spectrum of a chloroform solution of diphenyl ether has been shown by Purvis and McClelland (T., 1912, 101, 1517) to contain two bands, and we found a similar spectrum with the alcoholic solution.

The spectrum of diphenyl sulphide differs entirely from that of diphenyl ether; it contains no bands, but there are two extensions of the spectrum as with phenyl mercaptan.

The examination of the spectra of the foregoing showed that the substitution of sulphur for oxygen had resulted in the suppression of the phenol bands except in the case of the sodium salt of phenyl mercaptan, and even in this case the spectrum was altered considerably (compare Purvis, Jones and Tasker, *loc. cit.*).

The spectra of the vapours of phenol, diphenyl ether, phenyl mercaptan, and diphenyl sulphide were also examined, and it was found that whilst the spectrum of phenol vapour showed a large number of sharp bands, that of phenyl mercaptan vapour showed only two very feeble diffuse bands. Diphenyl ether vapour, on the other hand, showed two bands in almost the same position as the bands in the solutions, whilst the spectrum of diphenyl sulphide contained a number of sharp, narrow bands.

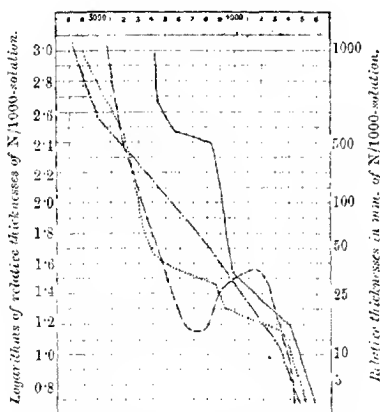
The vapour spectrum of phenol vapour is striking. In the neighbourhood of the melting point of phenol, more than seventy narrow, sharp bands could be counted between  $\lambda$  2800 and  $\lambda$  2500, and only a few were found outside this region.\* The largest number of bands was observed between  $36^\circ$  and  $50.5^\circ$ , and the following list shows the position of some of the principal bands at  $44^\circ$  and 765 mm. of pressure. The abbreviations are, as far as possible, those used by Purvis in his papers on vapour spectra

\* The vapour spectra were observed in a 200 mm. tube 21 mm. in diameter, the light of the cadmium spark being used. The tube was placed in an air-bath heated to the required temperature and maintained at this temperature for some time. Excess of the substance was used, and before taking a photograph the tube was opened to the air for an instant by means of a tap. Temperatures up to  $150^\circ$  were reached in this way.

(T., 1912, 101, 1520, etc.).  $\lambda$  2791 w., 2785 w., 2770 to 2766 w. band, 2756 to 2749 str. band, 2715 str., 2703 to 2694 str. band, 2689 to 2678 str. band, 2658 f.str., 2649 f.str., 2637 f.str., 2632 to 2628 str. band, 2626 to 2616 str. band, 2615 to 2610 str. band, 2604 w., 2602 w., 2593 w., 2581 w., 2531 f.str., 2520 w.; the rays are then transmitted to  $\lambda$  2220.

Most of the wider bands are really the effect of a number of very weak, sharp bands, which almost run together into one wider band. At higher temperatures this coalescence is more complete, and at 50° two of these bands are distinct, and have their heads

Oscillation frequencies.



Full curve : Phenyl mercaptan in alcohol.  
 Dash curve : Phenyl mercaptan with sodium ethoxide.  
 Dotted curve : Diphenyl sulphide in alcohol.  
 Dot and dash curve : Diphenyl disulphide in alcohol.

at  $\lambda$  3610 and  $\lambda$  3760. It is noteworthy that this is nearly the position occupied by the two solution bands of anisole (Baly and Ewbank, *loc. cit.*), and is almost identical with that of the bands of anisole vapour (Purvis and McClelland, T., 1912, 101, 1520).

Two narrow bands at  $\lambda$  2835 and  $\lambda$  2815 appear at 61° to 105°, and two more at  $\lambda$  2867 and  $\lambda$  2854 at 115° to 129°. At 105° almost all the sharp, narrow bands have coalesced to form one wide band from  $\lambda$  2820 and  $\lambda$  2430, which is almost identical in position with the single solution band of phenol.

The main feature of the vapour spectrum of phenyl mercaptan

is the strong general absorption. At  $43^{\circ}$  and 763 mm. pressure, two weak bands occur, extending from  $\lambda$  2870 to  $\lambda$  2859, and from  $\lambda$  2798 to  $\lambda$  2778 the rays being transmitted as far as  $\lambda$  2600. The position of these bands is in approximately the same position as the first extension of the spectrum of the alcoholic solution of this substance.

The spectrum of diphenyl ether vapour at  $81^{\circ}$  and 761 mm. pressure showed two weak bands, which were most marked at  $102^{\circ}$ , at which temperature they extended from  $\lambda$  2798 to  $\lambda$  2768, and from  $\lambda$  2710 to  $\lambda$  2690. At  $133^{\circ}$  there was one band from  $\lambda$  2798 to  $\lambda$  2590. In this case, also, the vapour and solution bands are in almost the same position.

Although the solution spectrum of diphenyl sulphide contains no bands, the vapour of this substance at 764 mm. showed a large number, which were most numerous at  $46^{\circ}$  and persisted to  $76^{\circ}$ . Amongst these bands the following were marked:  $\lambda$  2715 w., 2706 w., 2695 w., 2691 str., 2685 w., 2679 str., 2659 w., 2655 str., 2643 w., 2633 w., 2622 str., 2611 w., 2609 w., 2604 w., 2600 w., 2596 w., 2591 w., 2587 w.; general absorption begins at  $\lambda$  2440. At  $135^{\circ}$  only general absorption from  $\lambda$  2860 was observed. The vapour spectrum of diphenyl sulphide is therefore a banded spectrum, and there is some indication of grouping of the narrow bands between  $\lambda$  2695— $\lambda$  2679,  $\lambda$  2655— $\lambda$  2611, and  $\lambda$  2609— $\lambda$  2591. These positions correspond with the middle portions and points of inflexion of the spectrum of the solution.

In all the foregoing examples it is seen that the position of the bands of the spectra of the vapours corresponds with the position of the bands in the alcoholic solution or with the extensions of the solution spectra. The spectra of diphenyl sulphide are, from this point of view, particularly interesting, because in this case we have the extensions in the spectrum definitely associated with bands in the vapour spectrum. These extensions of the spectrum may therefore be considered as bands of extremely small persistency. The marked effect of the thiol group in suppressing the characteristic bands of benzene is similar to that of certain other substituents, which are assumed to possess "residual affinity," such as iodine and the nitro-group. A solution of iodobenzene gives no bands, and the single band of nitrobenzene is of very slight persistency.

We desire to express our thanks to the Research Fund Committee of the East London College for a grant towards the cost of this investigation.

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# CONTENTS.

## PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
LVIII.—The Latent Heats of Chloroform and Benzene and of their Mixtures Between 0° and 80°. By JAMES FLETCHER and DANIEL TYRER . . . . .	517
LIX.—The Relation Between the Absorption Spectra of Acids and their Salts. Part I. Sodium Salts. By ROBERT WRIGHT (1851 Exhibition Scholar) . . . . .	528
LX.—Metaphosphoric Acid and its Alkali salts. By ALFRED HOLT and JAMES ECKERSLEY MYERS . . . . .	532
LXI.—The Action of Chlorine on Thymol and on <i>m</i> -Cresol. By HORACE LESLIE CROWTHER and HAMILTON McCUMBE . . . . .	536
LXII.—The Constituents of the Oil of <i>Cytisus indicus</i> . By EDWIN ROY WATSON . . . . .	548
LXIII.—Studies on Cyclic Ketones. Part III. By SIEGFRIED RUHEMANN and STANLEY ISAAC LEVY . . . . .	551
LXIV.—Partially Methylated Glucoses. Part I. $\zeta$ -Monomethyl Glucose and $\gamma\zeta$ -Trimethyl Glucose. By JAMES COLQUHOUN IRVINE and JAMES PATTERSON SCOTT, M.A., D.Sc. (Carnegie Fellow) . . . . .	564
LXV.—Partially Methylated Glucoses. Part II. $\beta\gamma$ -Dimethyl $\alpha$ -Glucose and $\beta\gamma$ -Dimethyl $\beta$ -Glucose. By JAMES COLQUHOUN IRVINE and JAMES PATTERSON SCOTT, M.A., D.Sc. (Carnegie Fellow) . . . . .	575
LXVI.—Studies in the Diphenyl Series. Part IV. The Absorption Spectra of the Two Isomeric <i>o</i> -Dinitrobenzidines. By JOHN CANNELL CAIN, ALEXANDER KILLEN MACBETH, and ALFRED WALTER STEWART . . . . .	586
LXVII.—The Influence of the Constitution of Tertiary Bases on the Rate of Formation of Quaternary Ammonium Salts. Part I. By EBENEZER REES THOMAS . . . . .	594
LXVIII.—Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. Part I. Resolution of Phenylmethylethylazonium Iodide into Optically Active Components. By BAWA KANTAR SINGH . . . . .	604

LXIX.—The Formation of Cyclic Compounds from Derivatives of 2:2'-Ditolyl. By JAMES KENNER . . . . .	613
LXX.—The Vapour Pressures of the Lower Alcohols and their Azeotropic Mixtures with Water. Part I. Ethyl Alcohol. By RICHARD WILLIAM MERRIMAN, M.A. . . . .	628
LXXI.—The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part III. Solubility of Carbon Dioxide at Pressures lower than Atmospheric. By ALEXANDER FINDLAY and THOMAS WILLIAMS, B.Sc. (1851 Exhibition Science Bursar, University College of Wales, Aberystwyth) . . . . .	633
LXXII.—A New Iron Bacterium. By ERNEST MOORE MUMFORD . . . . .	642
LXXIII.—Gossypetin. By ARTHUR GEORGE PERKIN . . . . .	650
LXXIV.—Studies in the Camphane Series. Part XXXIV. Configuration of the Eight Oximino-derivatives of Camphorquinone. By MARTIN ONSLOW FORSTER . . . . .	664
LXXV.—Externally Compensated Hydroxyhydrazinohydrindene, its Derivatives, and Resolution into Optically Active Components. By DAVID HENRY PEACOCK . . . . .	666
LXXVI.—The Action of Ozone on Cellulose. Part III. Action on Beech Wood (Lignocellulose). By CHARLES DORÉE and MARY CUNNINGHAM . . . . .	677
LXXVII.—Experiments on the Walden Inversion. Part IX. The Interconversion of the Optically Active Phenylmethylcarbinols. By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH . . . . .	687
ANNUAL GENERAL MEETING . . . . .	700
PRESIDENTIAL ADDRESS . . . . .	713
OBITUARY NOTICES . . . . .	747

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.—

## PART I.

*Organic Chemistry.*

BURNELL (GEORGE A.). Notes on Mine Gas Problems . . . . .	755
JAMES (JOSEPH H.). Solvents for Acetylene . . . . .	756
SCHLECHTER (CARL WILLI). Preparation of Dimethylacetylene (Crotonylene) and Ethylacetylene from Carbides . . . . .	757
ENKLAAR (CORNELIS J.). $\Delta^{10}$ -H-patriene and Related Substances . . . . .	758
WILLSTÄTTER (RICHARD) and THEODOR WIRTH. Vinylacetylene . . . . .	759
SABATIER (PAUL) and ALPHONSE MAILHE. A Catalytic Method of Isomerisation of Alkyl Chlorides and Bromides . . . . .	760

# CONTENTS.

iii

	PAGE
BOESKEN (JACOB) (with C. E. KLAMMER and J. G. DE VOOGT). Trichloroethylene and Some of its Derivatives	i, 330
FOHNI (W.) and N. SOCHANSKI. Elimination of Water from Pinacolyl Alcohol. Tertiary Butylethylene	i, 331
BOESKEN (JACOB) and G. H. VAN SENDEN. Decomposition of Heptyl Alcohol at 220° in the Presence of Finely Divided Nickel	i, 331
LOCHINOV (N. A.). $\alpha$ -Oxide from Undecyl Alcohol	i, 332
LESPIEAU (ROBERT) and BRECH. Action of $\alpha$ , $\beta$ -Dichloroethyl Ether on Mixed Magnesium Derivatives	i, 333
ARBUZOV (ALEXANDER E.) and A. V. KARTASCHOV. Compounds of Ethyl Phosphite with Silver Haloids	i, 333
CEESNER DE CONINCK (WILLIAM) and ALBERT RAYNAUD. Uranium Formate	i, 333
MERCK (EMANUEL). Preparation of Halogen Formic Esters	i, 334
ESCALER (RICHARD) and HANS KOEPKE. Distillation and Sublimation of Ammonium Salts under Diminished Pressure	i, 334
BOESKEN (JACOB) (with P. HASSELBACH, W. J. P. PELLE, and (Mlle.) S. VAN DER TAS). Decomposition of Certain Acid Chlorides by Aluminium Chloride	i, 334
RYAN (HUGH) and JOSEPH ALGAR. Montanic Acid and its Derivatives	i, 335
BARRIER (PHILIPPE) and RENÉ LOQUIN. Action of Thionyl Chloride on Certain Lactones	i, 336
BARRIER (PHILIPPE) and RENÉ LOQUIN. Action of Thionyl Chloride on Certain Lactonic Acids	i, 337
ATWEIS (KARL VON) and M. SCHMIDT. $\gamma$ -Trichloro- $\beta$ -hydroxybutyric Acid and $\gamma$ -Trichloro- $\alpha$ -keto- $\beta$ -hydroxybutyric Acid	i, 338
ATWEIS (KARL VON) and M. SCHMIDT. The Constitution of the Chlorides of 1:2- and 1:3-Dicarboxylic Acids	i, 338
LOQUIN (RENÉ). Preparation of Tripeptidic and Terebic Acids	i, 341
BARRIER (PHILIPPE) and RENÉ LOQUIN. Attempts to Synthesise Monosubstituted Paraconic Acids	i, 341
KROLL & Co. Preparation of Strontium Cholate	i, 341
ANDERSON (ERNEST). Oxidation of Aldehydes by an Aqueous Solution of Bromine	i, 341
HARRIES (CARL D.). Glyoxal	i, 342
SENDEKENS (JEAN B.). Catalytic Preparation of Ketones	i, 342
STOKLASA (JULIUS), JOHANN SEBOH, and WENZEL ZIMONICKI. The Synthesis of Sugars by means of Radioactive Emanations	i, 342
FABENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of $\delta$ -Dimethylamino- $\Delta^2$ -isomylene and $\delta$ -Dimethylamino- $\Delta^2$ -butylene	i, 342
FABENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of $\delta$ -Dimethylamino- $\gamma$ -dimethylbutan- $\beta$ -ol	i, 342
FABENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of Amino- and Diamino-ketones of the Aliphatic Series	i, 343
MERCK (EMANUEL). Preparation of Urethanes of Tertiary Alcohols	i, 343
LOE (WALTER). Behaviour of Formamide Under the Influence of the Silent Electric Discharge. The Question of Nitrogen Assimilation	i, 343
MOLL VAN CHARANTE (JACOB). The Diamide of Sulphosubutyric Acid	i, 344
SPULTZENBERG (HUGO). Extraction of Glutamic Acid Hydrochloride and Betaine Hydrochloride from Molasses Residue	i, 345
SMOLE (ROBERT). Action of Sodium Hypobromite on Semicarbazide	i, 345
LAV (HEINRICH) and F. MANNCHEN. Salt- and Complex Salt-Formation with Amino- and Hydroxy-acetohydroxamic Acids	i, 346
ARBUZOV (ALEXANDER E.). New Method of Preparing Nitriles of the Aliphatic Series	i, 347
STROTHOLM (DANIEL). Chromates and Mercuric Cyanide	i, 347
WELLS (HOLACE L.). Potassium $\beta$ -Ferriocyanide	i, 347
TSCHIRVINSKI (PETR N.). Crystalline Form of Two Scandium Platinocyanides	i, 348
FOURBOIS (PIERRE). Magnesium Methyl Iodide	i, 348



	PAGE
GODCHOT (MARCEL) and FÉLIX TABOURY. The Catalytic Hydrogenation of Comphorone. Some New <i>cyclo</i> Pentane Hydrocarbons	i, 345
WILLSTÄTTER (RICHARD) and MICHAEL HEIDELBERGER. The <i>cyclo</i> Octane Series. VI. <i>cyclo</i> Octatetraene	i, 345
RADISCHE ANILIN- & SODA-FABRIK. [Preparation of <i>cyclo</i> Hexene]	i, 346
KUNCKELL (ERANZ) and GEORG ULEX. Rational Preparation of Some Benzene Homologues. II.	i, 350
CIAMICIAN (GIACOMO L.) and PAUL SILBER. Chemical Action of Light XXV. Antioxidations. III	i, 355
MENSCHUTKIN (BORIS N.) Influence of Substituents in Benzene on the Binary Systems. Substituted Benzene-Antimony Trihaloids.	i, 351
MENSCHUTKIN (BORIS N.) Influence of Substituents in Benzene on the Properties of the Binary Systems Formed by Substituted Benzenes and Antimony Trichloride or Tribromide.	i, 352
WOLFFENSTEIN (RICHARD) and OSKAR BÖTERS. The Catalytic Action of Mercury in Nitrations	i, 355
WILLSTÄTTER (RICHARD) and VICTOR L. KING. Hydrogenation of Aromatic Compounds by means of Platinum and Hydrogen. II. Dihydronaphthalene	i, 359
BLANKMA (JAN J.) Derivatives of <i>p</i> -Xylene	i, 359
WEDEKIND (EDGAR) and F. PASCHKE. Kinetics of Ammonium Salts	i, 365
HALBAN (HANS VON). The Kinetics of Ammonium Salts.	i, 368
MAILHE (ALPHONSE). Nitro-derivatives of Cresyl Oxides [Tolyl Ethers]	i, 362
MAILHE (ALPHONSE). Nitro-derivatives of Cresylene Oxides [Tolylene Oxides]	i, 365
FARBENFABRIKEN FORM. FRIEDR. BAYER & CO. Preparation of Halogenated Aminonaphtholsulphonic Acids	i, 365
ZINCSE (THEODOR) and JOH. MÜLLER. 3-Aminophenyl Mercaptan	i, 365
FROMM (EMIL) [with AQUILA FORSTER, ERITZ SCHÄFER, and BORIS VON SCHERSCHWITZKI.] Basic Properties of Sulphoxides and their Position Among the Organo-metallic Bases	i, 377
WITT (OTTO N.) and D. UERMENYI. Substituted Aryl Sulphonamides	i, 369
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. Preparation of <i>p</i> -Alkylalkoxyphenylaminoalkyl Sulphites	i, 368
FARBENFABRIKEN FORM. FRIEDR. BAYER & CO. Preparation of Aromatic Amino-alcohols	i, 368
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. Preparation of Esters of Nitroanthraquinonylanthranilic Acid	i, 369
STARK (OTTO) and O. GABEN. Meiquinonoids	i, 369
SABATIER (PAUL) and MARCEL MURAT. Direct Hydrogenation of the Phenylacetic Esters. Preparation of <i>cyclo</i> Hexylacetic Acid	i, 369
HAUSER (OTTO) and H. MUSCHNER. Esters of Cellulose with Benzoic Acid and its Derivatives	i, 369
DUPFLOK (ALEXIS). An Interesting Case of Dimorphism	i, 369
WOLFFENSTEIN (RICHARD) and W. PAAR. Nitration of Benzoic Acid in the Presence of Mercury	i, 369
WOLFFENSTEIN (RICHARD) and W. PAAR. 2:4:6-Trinitro- <i>m</i> -hydroxybenzoic Acid	i, 369
HELLER (GUSTAV) [with OTTO FRITSCH]. Action of Hydrogen Cyanide on <i>p</i> -Nitrobenzaldehyde	i, 369
FARBENFABRIKEN FORM. FRIEDR. BAYER & CO. Preparation of Carboxy-diarylhydrols	i, 369
AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION. Preparation of 2-Halogen-5-acylamino benzoylbenzoic Acid	i, 369
BOTGAULT (J.). $\alpha$ -Hydroxy- $\gamma$ -phenylcrotonic Acid. An Example of an Ether of a Ketone Hydrate	i, 369
WOLFFENSTEIN (RICHARD) and JOSEF ZELTZER. Preparation of Esters of Acetylsalicylic [ <i>o</i> -Acetoxybenzoic] Acid	i, 369
FARBENFABRIKEN FORM. FRIEDR. BAYER & CO. Preparation of Chloraanthraquinonecarboxylic Acids	i, 369

# CONTENTS.

v

	PAGE
HAHN (DOROTHY A.) and ANGIE G. ALLREE. Saturated $\beta$ -Ketonic Esters and their Derivatives	i, 367
MEYER (HANS) and KARL STRINER. A New Oxide of Carbon, $C_{22}O_4$	i, 368
SEMMER (FRIEDRICH W.) and FELIX RUSSE. Constituents of Essential Oils. [Degradation of the Diketone, $C_{15}H_{20}O_4$ , Obtained from Selinene]	i, 369
HALE (WILLIAM J.) and LAMBERT THORP. Studies in the <i>cyclo</i> pentadiene Series. III. Certain Derivatives of 5-Nitro-2:3-dibenzoyl- $\Delta^1:3$ - <i>cyclo</i> -pentadiene	i, 369
BAMBERGER (EUGEN) and EMIL REBER. Action of Hydrochloric and Hydrobromic Acids on 2:4-Dimethylquinol [2:4-Dimethyl- $\Delta^2:5$ - <i>cyclo</i> -hexadiene-4-ol-1-one]	i, 370
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. Preparation of Derivatives of <i>p</i> -Benzoquinone	i, 372
FAHRISCHE ANILIN- & SODA-FABRIK. Preparation of Chloroanthraquinones	i, 373
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. Preparation of 1-Halogen-2-aminoanthraquinones	i, 373
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. Preparation of Nitro- <i>p</i> -acyldiaminoanthraquinone	i, 373
FARBENFABRIKEN FORM. FRIEDR. HAYER & CO. Preparation of Dianthraquinonylthio-ethers	i, 373
HEPP (EDUARD), RUDOLF UBLENHUTH, and FRITZ RÖMER. Anthrallavone G	i, 374
ULMANN (FRITZ) and KARL LEWIG KLINGENBERG. 2-Methylanthraquinone	i, 374
KÖMPPE (GUSTAV) and S. V. HINTIKKA. Action of Carbon Dioxide on the Magnesium Compound of Fenchyl Chloride	i, 375
FARBENFABRIKEN FORM. FRIEDR. BAYER & CO. Preparation of Esters of Dibromo- $\beta$ -phenylpropionic Acid	i, 376
CHEMISCHE FABRIK VON KERESZTY, WOLF & CIE. Preparation of a Fenchyl Ester	i, 376
BUCHNER (EDUARD) and WILHELM WEIGAND. The Constitution of Camphene	i, 376
SEMMER (FRIEDRICH W.) and IRENE ROSENBERG. The Constituents of Etheral Oils. High-boiling Camphor Oil	i, 377
HILLEN (G. H.). Caoutchouc and Guttapercha Resins	i, 378
ROSSEN (A. VAN). The Viscous Transformation of Caoutchouc	i, 379
HARRIES (CARL D.) [with EWALD FÖRROBERT]. The Hydrohaloids of Artificial and Natural Caoutchoucs, and the Caoutchouc-like Substances Regenerated from Them	i, 380
SPENCE (DAVID). Theory of Vulcanisation	i, 381
KILIAN (HEINRICH). $\alpha$ - and $\beta$ -Anthrarin and on Crystallised Albumin from <i>Antiaris</i> Latex	i, 381
NIEBENSTEIN (MAXIMILIAN). Anthocyanin. III. An Anthocyanin like Oxidation Product of Emmanthane	i, 382
FISCHER (HANS) and HEINRICH RÖSC. Action of Sodium Methoxide on Bilirubin Acid, Bilirubin, and Hemibilirubin	i, 382
RYAN (HUGH) and R. FITZGERALD. The Identity of Euphinitone with Homopteroceptin	i, 383
NAVASSARY (EMANUEL). Optical Activity of Tannin	i, 383
GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE. [Preparation of Derivatives of Benzanthrone Containing Sulphur]	i, 383
VEREINIGTE CHININFABRIKEN ZIMMER & CO. Preparation of Homologues of Hydroquinone	i, 384
JONG (ANNE W. K. DE). Alkaloids of Javanese Coca [Erythroxyloxy novoguttatense]	i, 384
BOHRINGERS (C. F.) & SOHNE. Preparation of Therapeutically Valuable Double Salts from Morphine and Narcotine	i, 385
CHEMISCHE FABRIK VON FRIEDR. HEYDEN. Preparation of Morphine Esters of Alkyl- and Aryloxy-fatty Acids	i, 385
SCHULTZ (MAX). Alkaloids of Pareira Root	i, 385
HEYL (FREDERICK W.), F. E. HEPNER and SYLVESTER K. LOY. Zygadenine, the Crystalline Alkaloid of <i>Zygadenus intermedius</i>	i, 386

	PAGE
BACKER (HILMAR JOHANNES). Electrochemical Reductions. III. Reduction of Nitrosoamines	i, 354
WEISSGERBER (RUDOLF) [with O. HERZ, ARNO KLEMM and F. KRAFT]. Indole	i, 357
ARBUZOV (ALEXANDER E.) and V. M. TICHVINSKI. Preparation of Substituted Indoles by the Catalytic Decomposition of Hydrazones	i, 359
HOWITZ (JOHANN), HEDWIG FRAENKEL and ELSE SCHROEDER. 5-, 6-, and 8-Iodoquinolines, and Their Derivatives	i, 361
ZINCKE (THEODOR) and G. WEISSPECKING. 2- <i>op</i> -Dinitrophenylisoquinolinium Chloride and its Products of Transformation	i, 363
HOWITZ (JOHANN) and J. PHILIPP. Bromination of 6-Methylquinoline and 6-Quinolinaldehyde	i, 365
HOWITZ (JOHANN) and O. KÖPKE. 8-Quinolyl Ketones and their Derivatives	i, 367
FAHRWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of 9-Methylcarbazole	i, 369
HAFTZSCH (ARTHUR). Kehrman's Interpretation of Chromo-Isomeric Acridonium Salts as "Quinhydrone Salts" which Contain Hydroacridine	i, 371
MEYER (ANDRÉ). "Halochromism" of the Derivatives of Phenylisoxazolone and of the Iodogenides	i, 373
WÄHL (ANDRÉ) and C. SILBERZWEIG. Some Derivatives of the Methoxyphenylisoxazolones	i, 375
EKLEY (JOHN B.) and STILES CLINTON. Action of Acetic Anhydride on some Benzylideneanthranilic Acids. II.	i, 377
DÖHLER (W.) and BERTHOLD RASSOW. A Gelatinous Mercury Salt of an Organic Sulphonic Acid	i, 379
ARNDT (FRITZ). Aromatic $\beta$ -Thiocarbamides and Orthothiocarbonic Esters	i, 381
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of 6-Aminodiaminobenzene and 7-Aminodiaminobenzene 1-naphthol-3-sulphonic Acids with their Derivatives	i, 383
ARBUZOV (ALEXANDER E.) and V. M. TICHVINSKI. Catalytic Decomposition of Phenylhydrazine by Cuprous Salts	i, 385
PAWLEWSKI (BRONISLAW). A Process for the Preparation of New Colouring Matters and its Application	i, 387
FAHRWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of 1- <i>p</i> -Bromo-4-iodophenyl- and of 4-Bromo-1- <i>p</i> -iodophenyl-2 : 3-dimethyl-5-pyrazolone	i, 389
JOHNSON (TREAT B.) and BEN H. NICOLET. Hydantoins. XXI. Action of Ammonium and Potassium Thiocyanates on $\alpha$ -Amino-acids	i, 391
KÖNIG (WALTER) and R. SCHIECKENBACH. The Reactivity of the $\beta$ -Unsaturated Pyrrole Ring. III. Action of Cyanogen Bromide and Pyridine on Indoles	i, 393
KALLE & Co. [Preparation of 4-Chloro-5-bromoanisole]	i, 395
FAHRWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of 5 : 6 : 5' : 6' Tetrachloroindigotin	i, 397
FAHRWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Dinitro-1 : 1'-dianthrindiol	i, 399
FAHRWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of $\alpha$ -Methylsulphites of Substituted Aminoarylpyrazolones	i, 401
JOHNSON (TREAT B.) and EDWARD F. KOHMANN. Pyrimidines. LIX. Barbituric and 2-Thiobarbituric 5-acetic Acids	i, 403
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of Azinobis-Triazole-compounds in the Anthraquinone Series	i, 405
KELLER (K.). Polymeric Indoles	i, 407
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of Formaldehyde Derivatives of Xanthine and its Substitution Products	i, 409
SCHADE (HEINRICH) and E. BODEN. The Anomalies in the Solubility of Uric Acid (Colloidal Uric Acid)	i, 411
JOHNS (CARL O.). Purines. VIII. 2 : 8-Dihydroxy-1 : 9-dimethylpurine and 2-Hydroxy-6 : 9-dimethylpurine	i, 413

	PAGE
VERNET (CAMILLE G.). Azomethines and Azo-dyes	i, 405
BEAND (KURT) and ADOLF WIRSING. Thiophenols. III. <i>pp'</i> -Azophenyl Methyl- and <i>pp'</i> -Azophenyl Ethyl-sulphide	i, 406
MÜHLAU (RICHARD) [with JOHANNES MARTEL]. The Lakes of Hydroxylic Dyes	i, 407
KATLE & CO. Preparation of Acetyl Derivatives of Aminocazobenzene, its Homologues and Analogues	i, 408
CHICK (MISS HARRIETTE) and CHARLES J. MARTIN. Density and Solution Volume of Certain Proteins	i, 409
AMERHOLDEN (EMIL) and DIONYS FUCHS. The Amount of <i>L</i> -Tyrosine in Proteins and the Accuracy of its Estimation	i, 409
PATERNÒ (EVANUELE) and FLORENTIN MEDIGRECEANU. Colloidal Solutions. I. Certain Metallic Peptonates	i, 409
FISCHER (HANS) and ERICH BARTHOLOMÄUS. Porphyrinogen	i, 409
DEZANT (SERAFFINO). Pepsin. II.	i, 410
KITA (G.). Some Properties of Koji-diasase	i, 410
BOUDRILOTT (EMIL) and J. COIRRE. The Reversibility of the Ferment Action of Emulsin	i, 410
ROSENTHALER (LEOPOLD). Hydrolysis of Amygdalin Under the Influence of Emulsin	i, 411
ROSENTHALER (LEOPOLD). Distribution of Emulsin-like Enzymes.	i, 411
CHODAT (ROBERT) and K. SCHWEIZER. Oxydases. VI. Tyrosinase is also a D-aminidising Enzyme	i, 411
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Derivatives of Nitrohydroxy- and Aminohydroxy-arylsarbinic Acids Containing Sulphur	i, 412
KARBER (P.). Aromatic Arsenic Compounds. IV. Preparation of 3-Nitro-4-dimethylamino-phenylarsinic Acid and of 3-Nitro-4-hydroxyphenyl-arsinic Acid	i, 412
KARBER (P.). Aromatic Arsenic Compounds. III. Trinzoarylsarbinic Acids and Some of their Derivatives	i, 412
ROSENTHAL (ARTHUR) and ROBERT BIERCKEL. Iso- and Hetero-poly-salts. VIII. Alkylarsinomolybdates	i, 413
BART (HEINRICH). Preparation of Organic Arsenic Compounds	i, 413
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Unsymmetrical Arseno-compounds	i, 413
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Aromatic Arseno-compounds	i, 416
CHEMISCHE FABRIK VON FRIEDR. HEYDEN. Preparation of Aromatic Stilbinic Acids	i, 416
CHEMISCHE FABRIK VON FRIEDR. HEYDEN. Preparation of Nuclear Substituted Mercury Derivatives of Aromatic Hydroxy-acids	i, 417

### *Physiological Chemistry.*

HIEZ (OTTO). The Influence of Phosphorus on Respiratory Metabolism	i, 417
CHAMPE (WILHELM) and HAROLD PRINGLE. The Coagulation of Blood	i, 417
STASSANO (HENRI). The Plasma of Propeptone	i, 418
BROHA (GISEPPE). The Transference of the Digestion Products of Proteins from the Mother to the Foetus	i, 418
EVANS (C. LOVATT). The Influence of Nutrition on the Amylase Content of Human Saliva	i, 418
KNOFF-LENZ (ERICH VON) and ERNST P. PICK. The Behaviour of Plastins in the Animal Body. I. The Relationships of Plastins to Peptone Poisoning	i, 419
AUERBACH (FRIEDRICH) and HANS PICK. Pancreatic Digestion	i, 419
ALEXANDROWICZ (JERZY STANISLAW). Comparative Physiology of Digestion. VI. Cellulose and Cellulose-dissolving Enzymes in the Hepatopancreas of the Snail ( <i>Helix pomatia</i> )	i, 419
AMERHOLDEN (EMIL). The Synthetic Powers of the Organism of the Dog	i, 419

	PAGE
ABDERHALDEN (EMIL) and ARNO ED. LAMPÉ. Action of Ammonium Salts, Glucosamine and Gelatin on the Nitrogen Balance . . . . .	i, 420
FISCHER (GUSTAV). Utilisation of Calcium and Phosphoric Acid Compounds by the Animal Organism . . . . .	i, 420
ABDERHALDEN (EMIL) and ARTHUR WEIL. Comparative Investigations on the Content of Amino-acids in the Different Constituent Parts of the Nervous System. II. The Amino-acids of the Grey and White Substance of the Brain . . . . .	i, 422
GRODEK (JULIUS) and ERNST J. LESSER. The Action of the Diastatic Enzyme on the Glycogen within the Cells . . . . .	i, 420
LESSER (ERNST J.). The Behaviour of the Glycogen of the Frog in Anoxibiosis and Restitution. III. . . . .	i, 420
HENNING (PERCY T.). Comparative Anatomy and Physiology of the Pituitary Body . . . . .	i, 421
GAVIN (W.). The Effects of the Administration of Extracts of the Pituitary Body and Corpus Luteum to Milch Cows . . . . .	i, 421
SCHÄFFER (EDWARD A.). The Effect of Pituitary and Corpus Luteum Extracts on the Human Mammary Glands . . . . .	i, 421
ROAF (HERBERT E.). The Liberation of Ions and the Oxygen Tension of Tissues during Activity . . . . .	i, 421
MINES (GEORGE R.). The Summation of Muscular Contractions . . . . .	i, 422
HILL (ARCHIBALD V.). The Energy Degraded in the Recovery Processes of Stimulated Muscles . . . . .	i, 422
JONA (THEMISTOCLE). The Extractives of Muscle. III. . . . .	i, 422
WEIßHARDT (WOLFGANG) and ERWIN SCHWENK. Products of Protein Cleavage which Produce Fatigue, and their Influence . . . . .	i, 422
CHOCQUARD (LOUIS). Physiological Permeability of Cells. V. Narcosis of Lipoid-rich and Lipoid-poor Tissues of the Same Kind . . . . .	i, 423
BERTHARD (GABRIEL) and HENRI AGUILHON. The Presence of Boron in the Animal Series . . . . .	i, 423
MAYER (ANDRÉ) and GEORGES SCHAFFER. The Composition of the Tissues with Respect to Non-volatile Fatty Acids and Cholesterol, and the Possible Existence of a "Lipocytic Constant" . . . . .	i, 424
MOYCHO (VENCESLAS). The Action of Ultra-violet Rays on the Ear of the Rabbit . . . . .	i, 424
GROSSER (PAUL). The Influence of Heat on the Physico-chemical Behaviour of Human Milk, Cow's Milk, and Butter-milk . . . . .	i, 424
BARICKOW (MAX). The Therapeutic Action of Yeast on the Alimentary Multiple Polyncuritis of Guinea-pigs and Pigeons . . . . .	i, 425
ROLLY (FR.) and FR. OFFERMANN. The Behaviour of Blood Sugar in Normal and Pathological Cases. VI. Blood-sugar Content in Cases of Anemia, Liver, Intestinal and Other Diseases . . . . .	i, 425
MEDIGRECEANT (FLORENTIN). The Manganese Content of Transplanted Tumours . . . . .	i, 425
LEHMANN (KARL R.). The Influence of Vapours of Technical Importance on the Organism. XXXII and XXXIII. Amyl Acetate and cyclo-Hexanyl Acetate . . . . .	i, 425
BICKEL (ADOLF) and MICHAEL PAVLOV. The Influence of Certain Cardiac Medicaments on the Electrocardium Curve . . . . .	i, 426
KONSCHEGG (ARTHUR VON). The Relationship between Heart Drugs and the Physiological Action of Cations . . . . .	i, 426
CANNON (WALTER B.) and HENRY LYMAN. The Depressor Effect of Adrenaline on Arterial Pressure . . . . .	i, 426
BIERRY (HENRI) and (Mlle.) LUCIE FAXHARD. Adrenaline and Glycemia . . . . .	i, 426
CLOETTA (MAX). [Physiological] Action of Scopolamine . . . . .	i, 426
BOEHM (RUDOLF). The Action of Veratrine and Protoveratrine . . . . .	i, 426
SKORCZEWSKI (W.) and J. SOHN. The Behaviour in the Organism of 2-Phenylquinoline-4-carboxylic Acid (Atophan) . . . . .	i, 427
DALMIER (R.). Action of Arseno-aromatic Compounds ("606" and Neosalvarsan) on the Hemoglobin of the Blood . . . . .	i, 427

*Chemistry of Vegetable Physiology and Agriculture.*

	PAGE
HOFFMANN (CONRAD). Protein and Phosphorus Content of <i>Azotobacter</i> Cells . . . . .	i, 427
KOZNIŃSKI (TADRUSZ). The Chemical Composition of Tubercle bacilli . . . . .	i, 428
BERTHELOT (ALBERT). Protein vulgaris Considered as a Producer of Indole . . . . .	i, 428
BOKORSY (THOMAS). Influence of Cesium, Rubidium, and Lithium Salts on Yeast as Compared with Potassium and Ammonium . . . . .	i, 428
BOUCHERLOT (ÉMILE), HENRI HÉRISSEY, and MARC BRIDEL. Biochemical Synthesis of Alkyl Glucosides ( $\alpha$ -Glucosides) by means of $\alpha$ -Glucosidase: $\alpha$ -Methyl Glucoside. Destruction of the $\alpha$ -Glucosidase in a Strongly Alcoholic Medium . . . . .	i, 428
HASELHOFF (EMIL). Action of Boron Compounds on the Growth of Plants . . . . .	i, 429
MAQUENNE (LÉON) and EM. DEMOUSSEY. The Value of the Chlorophyll Coefficients and their Relation to the Real Respiratory Coefficients . . . . .	i, 429
PALLADIN (VLADIMIR I.) and Z. N. TOLSTAJA. Absorption of Oxygen by the Respiratory Chromogens of Plants . . . . .	i, 430
ANDRÉ (GUSTAVE). The Migration of Mineral Constituents and the Displacement of These Constituents in Leaves Immersed in Water . . . . .	i, 431
SIMON (FRIEDRICH). The Germination of Seeds which have been Chemically Treated and Exposed to Light . . . . .	i, 431
BABY (JOHANNA). Alleged Constant Occurrence of Iodine in Cells . . . . .	i, 431
FOSSE (ROBERT). Formation of Carbamide by Higher Plants . . . . .	i, 432
MIRANDE (ROBERT). Presence of Callose in the Membrane of the Marine Siphonaceous Alge (Siphonales) . . . . .	i, 432
BUEMANN (JAMES). Influence of Temperature on the Development of Active Principles in Some Medicinal Plants . . . . .	i, 432
WEHMER (CARL). Production of Oxalic Acid by <i>Aspergillus niger</i> . . . . .	i, 432
LEWIN (LOUIS). <i>Calotropis procera</i> . A New Digitalis-like Drug . . . . .	i, 432
FALK (K. GEORGE). Enzyme Action. IV. Occurrence of a Urease in Castor Beans . . . . .	i, 433
WINTERSTEIN (ERNST) and M. A. JEGOROV. Constituents of the Seeds of <i>Croton tiglium</i> . . . . .	i, 433
HERRMANN (E.). The Acids of Fungi . . . . .	i, 433
WINTERSTEIN (ERNST), C. REUFER, and R. KOROLEV. Composition of Some Fungi, and the Products of Their Autolysis . . . . .	i, 433
BRIDEL (MARCE). The Presence of Gentiopictin, Gentianose, and Sucrose in the Fresh Roots of <i>Gentiana panchata</i> . . . . .	i, 434
KOZYTSKIY (S.), ELISE HUBERNEY, and A. SCHIFFMAYR. Formation of Acetaldehyde during the Anaerobic Respiration of Poplar Blossom . . . . .	i, 434
TSCHIRCH (ALEXANDER) and M. RUSZKOVSKI. A New Rhubarb from Altai . . . . .	i, 434
SCHRÖDER (F.). The Oil Seed of <i>Nimera Americana</i> , L. . . . .	i, 434
KYLIN (HARALD). Biochemistry of Sea Weeds . . . . .	i, 435
PANTANELLI (ENRICO) and G. SERVINI. Nutrition of Green Plants with Ammonium Salts . . . . .	i, 435
SEIDLER (LEOPOLD). Changes of Phosphoric Acid in Plants at Different Periods of Growth and with Different Phosphorus Manures . . . . .	i, 435
GILB (P. L.) and C. N. AGERTON. The Significance of the Lime-Magnesia Ratio in Soil Analyses . . . . .	i, 436
LEOPOLD (G. H.). Weathering of Soil . . . . .	i, 436
SEKI (TOSUAKO). Two Volcanogenic Loams from Japan . . . . .	i, 436

## PART II.

*General and Physical Chemistry.*

	PAGE
FALK (K. GEORGE). Change in Refractive Index with Temperature. III.	ii, 251
AUWERS (KARL VON). The Spectrochemistry of Compounds with a <i>gem</i> -Dialkyl Group.	ii, 261
KLEIN (FRITZ). Atc and Spark Spectrum of Lead.	ii, 262
WOOD (ROBERT W.). Selective Dispersion of Mercury Vapour at the $\lambda=2536$ Absorption Line.	ii, 262
LUTHER (ROBERT) and ANDREAS NIKOLOPOULOS. Relationship between the Absorption Spectrum and the Constitution of Complex Cobaltaniline Salts.	ii, 263
JHELECKI (JEAN) and VICTOR HENRI. Quantitative Investigation of the Absorption of Ultra-violet Rays by the Fatty Acids and their Esters in Aqueous and Alcoholic Solutions.	ii, 264
MEYER (RICHARD). Spectrographic Studies in the Anthraquinone Group.	ii, 264
MASSOL (GUSTAVE) and A. FAYON. Absorption Spectra of Fluorescein, Eosin, Erythrosin, and Rose-Bengal in the Visible and Invisible Regions.	ii, 264
HANTZSCH (ARTHUR) and ISRAEL LIFSCHITZ. Optical Investigations of Diazo-compounds.	ii, 264
KAUFFMANN (HUGO). The Theory of Fluorescence.	ii, 264
STARK (JOHANNES). The Theory of Fluorescence.	ii, 264
KAUFFMANN (HUGO). The Theory of Fluorescence.	ii, 264
PLONIKOV (JOH.). [Rotation Dispersion]	ii, 265
BOLL (MARCEL). Energy Absorbed and Mass Formed in a Photochemical Reaction.	ii, 265
WASSILJEWA (ALEXANDRA). Photochemical Behaviour of Colloidal Tungstic Acid.	ii, 265
WEIGERT (FRITZ). The Activation of Oxygen by Radiation.	ii, 266
HENRI (VICTOR) and MARC LANDAU. Absorption of the Ultraviolet Rays by Acetylene.	ii, 267
BERTHELOT (DANIEL) and HENRY GAUDECHON. The Inversion of Sucrose by Ultraviolet Rays.	ii, 267
BERTHELOT (DANIEL) and HENRY GAUDECHON. A Levulose Actinometer for Ultraviolet Rays. Influence of Concentration on the Rate of Photochemical Action.	ii, 267
MEYER (STEFAN). The Most Recent Value for the Atomic Weight of Radium.	ii, 267
HÖNIGSCHMID (OTTO). Revision of the Atomic Weight of Radium by Analysis of Radium Bromide.	ii, 268
HASCHKE (EDUARD) and OTTO HÖNIGSCHMID. The Purity of the International Radium Standard.	ii, 268
RUTHERFORD (ERNEST) and H. ROBINSON. Heating Effect of Radium and its Emanation.	ii, 269
DUANE (WILLIAM) and OTTO SCHREUR. Decomposition of Water by $\alpha$ -Rays.	ii, 270
DANYSZ (JEAN). The $\beta$ -Rays of Radium- <i>B</i> , - <i>C</i> , - <i>D</i> , - <i>E</i> .	ii, 270
RUSSELL (ALEXANDER S.). The Penetrating Power of the $\alpha$ -Rays of Radium- <i>C</i> .	ii, 270
KALLAN (ANTON). The Chemical Action of Penetrating Radium Rays. V. Influence of Penetrating Rays on Sterilised Aqueous Sucrose Solutions.	ii, 270
SCHWEIDLER (EGON VON). Theory of the Concentration Variations in Radioactive Solutions.	ii, 271
KOFLEK (MARTIN). The Solubility of Radium Emanation in Water as Regards its Dependence on the Temperature.	ii, 271
JACOT (E.). A Relation between Ionisation by Cathode Rays and Certain Chemical Effects.	ii, 271

# CONTENTS.

xi

	PAGE
HUTTON (FRANK). Positive Ionisation Produced by Platinum and by Certain Salts when Heated	ii, 272
SHEARD (CHARLES). Ionisation Produced by Heated Salts	ii, 272
TANATAR (SERASTIAN M.) and E. BURKBER. Separation of Corpuses in Chemical Reactions	ii, 273
PANETH (FRITZ). A New Method for Concentrating Polonium	ii, 273
HUGLEY (CHARLES FREDERICK). Solubility of the Active Deposit of Thorium in Various Solvents	ii, 273
MC COT (HERBERT N.) and CHARLES H. VIOL. The Chemical Properties and Relative Activities of the Radio-products of Thorium	ii, 274
KOLOWRAT (LÉON). Tables of Radioactive Constants	ii, 274
RUSSELL (ALEXANDER S.). Periodic System and Radio-elements	ii, 274
SODDY (FREDERICK). Radio-elements and the Periodic Law	ii, 275
FATAJS (KASIMIR). The Position of the Radio-elements in the Periodic System	ii, 276
FATAJS (KASIMIR). Radioactive Changes and the Periodic System of the Elements	ii, 277
SWINNE (RICHARD). Some Relations between the Radio-elements giving $\alpha$ -Rays	ii, 277
FATAJS (KASIMIR). A Relation between the Kind of Radioactive Change and the Electrochemical Behaviour of the Resulting Radio-element	ii, 277
KAMBERGER (MAX) and KARL KRUSE. The Radioactivity of the Mineral Springs of Tyrol. IV.	ii, 278
GRENGG (R.). The Radioactivity of the Mineral Springs of Tyrol. IV.	ii, 278
KIRBY (PAUL J.) and JAMES E. MARSH. Electrical and Chemical Effects of the Explosion of Azoinide	ii, 278
STRETT (Hon. ROBERT J.). Duration of Luminosity of Electric Discharge in Gases and Vapours	ii, 279
WATSON (HERBERT E.). Electrical Discharge in Helium and Neon	ii, 279
KOENIGSBERGER (JOHANNES) and G. GOTTSTEIN. The Hall Effect	ii, 280
CHERNER (FRITZ). The Changes in the Electrical Resistance of Wires which have been Drawn and Subjected to Torsion, and also of Drawn and Twisted Wires on Warming: Gold, Silver, Copper, Nickel, and Iron	ii, 280
LORENZ (RICHARD). The Theory of Electrolytic Ions. VI. The Conductivity of Pure Water	ii, 281
SHARFFER (E. J.) and HARRY C. JONES. Conductivity, Dissociation, and Temperature-coefficients of Conductivity of Certain Inorganic Salts in Aqueous Solution, as Conditioned by Temperature, Dilution, Hydration, and Hydrolysis	ii, 282
PRAPOLOGO (UGO). Citrophosphate Solutions. II. Electrical Conductivity of Aqueous Solutions of Citric Acid and Phosphoric Acid	ii, 282
SHAW (LEON IRWIN). Electrical Conductance of Non-aqueous Solutions	ii, 283
SACHANOV (ALEXANDER NICOLAEVITSCH). Abnormal Electrical Conductivity Changes. IV.	ii, 288
GOLDSCHMIDT (HEINRICH) and HANS KEE. GEINL. The Addition of Alkyl Halogens to Thiocarbamides	ii, 284
FISCHER (FRANZ) and OTTO PRIESS. The Reduction to Hydrogen Peroxide of Oxygen Dissolved under Pressure	ii, 285
KOHLSCHEUTER (VOLKMAR) and THEODOR TOROFF. The Form of Electrolytically Deposited Metals. I. Silver-black	ii, 285
KOHLSCHEUTER (VOLKMAR), THEODOR TOROFF, and W. PFANDER. The Form of Electrolytically Deposited Metals. II. Silver Deposited by Metals	ii, 286
KOHLSCHEUTER (VOLKMAR) and HERMANN SCHACHT. The Form of Electrolytically Deposited Metals. III. The Influence of Foreign Substances on the Deposition of Silver	ii, 287
KOHLSCHEUTER (VOLKMAR). The Form of Electrolytically Deposited Metals. IV. The Deposition of Silver from Solutions of Complex Salts	ii, 287
OXLEY (A. E.). Variation of Magnetic Susceptibility with Temperature. II. Aqueous Solutions	ii, 288



	PAGE
COTTON (A.) and HENRI MOUTON. Magnetic Double Refraction and Chemical Constitution	ii, 288
BRONIEWSKI (WITOLD). The Critical Points of Iron	ii, 288
HILBERT (SIEGFRIED) and FRITZ HERMANN. The Thermoelectric Properties of Some Irreversible Nickel and Manganese Steels	ii, 289
HENNING (FRITZ). The Gas Thermometer as the Basis for High-temperature Measurements	ii, 289
BAHR (FRITZ). A Simple Method for Maintaining Constant Temperatures in the Region of the Room Temperature	ii, 290
HÄUSER (OTTO) and W. SIEGER. The Specific Heat of Bismuth Oxide	ii, 290
JOHNSTON (JOHN) and LEASON H. ADAMS. Effect of High Pressures on the Physical and Chemical Behaviour of Solids	ii, 290
LE CHATELIER (HENRI) and (Mlle.) CAVAIGNAC. Fusibility of Natural Fats	ii, 291
PASCAL (PAUL) and LÉON NORMAND. Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. II. Mixtures containing Unsymmetrical Constituents	ii, 292
BLOCK (ERNST AUGUST). The Fusion Curves of Several Substances	ii, 292
JÄRVINEN (K. K.). Molecular Attraction	ii, 293
ARDEL (EDMOND VAN). The Latent Heat of Vaporisation of Metals	ii, 294
MARCKLIN (RENÉ). Mechanism of Evaporation	ii, 294
BRÖNSTED (JOHANNES N.). Chemical Affinity. VIII. Crystalline Change of the Alkali Salts	ii, 295
GRUWITSCH (L.). Fractional Distillation with Steam	ii, 295
REFF (OTTO) and EWALD GERSTEN. Trifluorocarbide (Cementite), $\text{Fe}_3\text{C}$	ii, 296
VANZETTI (BARTOLO L.). Heat of Formation of Additive Organic Compounds. I. Picrates	ii, 296
ROTH (WALTER A.) and RICHARD STORMER. Physico-chemical Investigations with Aromatic Stereoisomeric Acids. I.	ii, 296
PHILPOTTE (MAURICE). Densities at the Critical Point	ii, 298
JURISCH (KONRAD W.). Pressure, Density, and Expansion of Saturated Water Vapour	ii, 298
JURISCH (KONRAD W.). The Influence of Dissociation on the Density of Saturated Water Vapour	ii, 298
JURISCH (KONRAD W.). The Influence of Dissociation on the Expansion of Saturated Water Vapour	ii, 298
WALDEN (PAUL) and RICHARD SWINNE. The Temperature-coefficient of the Molecular Surface Energy and the Molecular Cohesion	ii, 299
JONES (WILLIAM J.). Dimensions of the Surface Energy of Solid Substances	ii, 300
MATTHEWS (ALBERT P.). Method of Determining " $\alpha$ " of van der Waals' Equation from the Surface Tension	ii, 300
KLEEMAN (RICHARD D.). Properties of a Liquid Connected with its Surface Tension	ii, 301
FOL (J. G.). Determination of the Viscosity of Camphene Solutions	ii, 301
SOKRAU (WALTHER). Relationship between Molecular Weight and Turbulence Viscosity Constant	ii, 301
ROHLAND (PAUL). The Adsorptive Power of the Hydroxides of Silicon, Aluminium, and Iron. VI.	ii, 302
RAKOVSKI (ADAM V.). Adsorption. VIII. Adsorption by Starch in Mixed Solutions	ii, 302
RAKOVSKI (ADAM V.). Adsorption. IX. Adsorption and Hydrolysis	ii, 303
REBOUL (G.). Influence of the Geometric Form of Solids on the Chemical Reactions which they Undergo	ii, 303
REBOUL (G.). Capillary Phenomena in Gases. Extension of Laplace's Formula to the Contact Solid-gas	ii, 303
FOUARD (EUGÈNE). The Differential Tonometry of Solutions and the Theory of Arrhenius	ii, 304
LIEBERGANG (RAPHAEL E.). [Stratified Systems]	ii, 304
GOLODETZ (A.). New Apparatus for Quantitative Dialysis	ii, 304

# CONTENTS.

xiii

	PAGE
PASCAL (PAUL) and LÉON NORMAND. Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. I. . . . .	ii, 304
FEDOROV (EVGRAP F.). Chemical and Crystal Molecules . . . . .	ii, 305
BERTHOUD (A.). Formation of Crystal Faces . . . . .	ii, 305
FEDOROV (EVGRAP F.). Chemical Analogies of Substances Showing a Crystallographic Relation to Potassium Sulphate . . . . .	ii, 306
FORT (MORRIS). Efflorescence of Crystals under Water . . . . .	ii, 306
MELOZIKOVSKI (A.). Liquid Crystals of Ammonium Oleate . . . . .	ii, 306
BENJEDJES (CARL). Nature of the Electrical Synthesis of Colloids . . . . .	ii, 307
WEIMANN (P. P. VON). [Preparation of a Dispersoid Solution of any Substance]. . . . .	ii, 307
FRANK (JOSEF). Physical Properties of Colloidal Solutions . . . . .	ii, 307
KOLOSOVSKI (NICOLAS A.). Thermo-chemical Researches on Solution and their Bearing on Theoretical Considerations concerning the Relations between the Chemical Properties of Solutions . . . . .	ii, 308
BERTHOUD (A.). Influence of Temperature on the Velocity of Chemical Reactions . . . . .	ii, 309
KLING (ANDRÉ) and DANIEL FLORENTIN. Action of Low Temperatures on Explosives . . . . .	ii, 309
COLIN (H.) and A. SÉNÉCHAL. The Oxidation of Complex Cobalto-organic Compounds . . . . .	ii, 310
KRAPIVIN (SERGIUS). Velocity of the Reaction between Sodium Thiosulphate and Sodium Bromoacetate . . . . .	ii, 310
LINHART (GEORGE A.). Hydrolysis of Metallic Alkyl Sulphates . . . . .	ii, 310
ROSANOFF (MARTIN A.) and H. M. POTTER. Re-investigation of the Velocity of Sugar Hydrolysis. II. The Role of Water . . . . .	ii, 311
HIGGINS (SYDSEY H.). Action of Neutral Salts on Bleaching Solution . . . . .	ii, 311
FORT (MORRIS). Neutral Salt Reactions. II. A Double Neutral Salt Reaction and the Action of Glander's Salt on Wool . . . . .	ii, 311
BIDDLE (HENRY C.). Colour Changes Among Dyes of the Triphenylmethane Series as Influenced by the Hydrogen Ion Concentration of Acids of Different Dissociation Constants . . . . .	ii, 311
HAUBAN (HANS VON) and ALEXANDER KIRSCH. Xanthic Acid and the Kinetics of its Decomposition . . . . .	ii, 312
COLLINS (HAWKSWORTH). Structure of Some of the Elements . . . . .	ii, 313
CLARKE (FRANK W.). Twentieth Annual Report of the Committee on Atomic Weights. Determinations published during 1912 . . . . .	ii, 313
GUARESCHI (LELIO). A New Source of Error in the Determination of Atomic Weights . . . . .	ii, 313
GRAEBER (CARL). The Development of Arrhenius's Theory . . . . .	ii, 313
MEYER (RICHARD). What are Bases and Acids? . . . . .	ii, 313
SOUTHERDEN (FRANK). Gas Generator . . . . .	ii, 314
WILEY (S. W.). A Redox Condenser . . . . .	ii, 314
PERRINS (A. E.). A New Form of Laboratory Extraction Apparatus . . . . .	ii, 314
MACNIDER (G. M.). A Modified Extraction Apparatus . . . . .	ii, 314
SMITH (NATHAN). A Useful Valve . . . . .	ii, 314
PARKER (C. E.). New Separating Funnel . . . . .	ii, 315

## Inorganic Chemistry.

COHEN (ERNST) and J. F. KROGER. Physico-chemical Studies on Tellurium. I. . . . .	ii, 315
KOENIG (A.) and E. ELON. After-Luminosity in Pure Nitrogen after the Passage of Electric Discharge . . . . .	ii, 316
SCHULT (HON ROBERT J.). The Chemically Active Modification of Nitrogen . . . . .	ii, 316

	PAGE
FRIEDRICHS (FRITZ). Extraction with Liquefied Gases and the Ammonolysis of Hydrazine Sulphate	ii, 316
FISCHER (FRANZ) and EMIL HENKE. Chemistry of the Formation of Nitric Oxide in the High Tension Arc. II.	ii, 317
BRINER (EMIL) and (MILC.) Z. PYLKOV. Formation and Properties of Nitrosyl Chloride	ii, 317
SPONGI (UMBERTO). Borates. The System $B_2O_3-(NH_4)_2O-H_2O$ at $30^\circ$ . II.	ii, 318
SMITS (ANDREAS) and KUBB ENDELL. The System $SiO_2$	ii, 318
KITTL (ERWIN). The Crystallising Power of Silicates	ii, 319
PUSCHIN (NIKOLAI A.) and A. V. BASKOV. Equilibria in Binary Systems of Fluorides	ii, 319
DHAR (NILRATAN). Double and Complex Salts. I.	ii, 319
BRINKE (EMIL) and A. KUHN. The Transformation Undergone by Heated Calcium Carbide	ii, 320
BITZ (HUGO). Supposed Occurrence of a Peroxide in Calcium Hydroxide, which has been Exposed to Air, and in Aragonite	ii, 320
GASSMANN (THEODOR). Preparation of a Complex Salt of the Apatite Type and its Bearing on the Formation of Bone	ii, 320
AMBRONN (H.). Dispersion of the Birefringence of Mixed Crystals of Strontium and Lead Dithiourates	ii, 321
MIELEITNER (K.) and H. STEINMETZ. The Hydrate and Ammoniate of Glucinum Chloride	ii, 321
SIEVERTS (ADOLF) and E. BERGNER. The Solubility of Sulphur Dioxide in Molten Copper Alloys	ii, 321
BERRY (ARTHUR J.). Volatilisation of Certain Binary Alloys in High Vacua	ii, 322
MYERS (JAMES E.) and JAMES B. FIRTH. The Reduction of Solutions of Copper Sulphate by Sodium Hypophosphite and Sodium Hyposulphite	ii, 322
MEYER (RICHARD J.) and J. WUORINEN. The Purification and Atomic Weight of Yttrium	ii, 323
JAMES (CHARLES). The Rare Earths of the Carolina Monazite Sands	ii, 323
FEDOTÉV (P. P.) and V. L. ILJINSKY. The Electro-Metallurgy of Aluminium	ii, 324
SCALA (ALBERTO). Action of Distilled Water on Pure Aluminium. II.	ii, 325
RUFF (OTTO) and EWALD GRESTEN. The Carbides of Manganese and Nickel	ii, 325
GUILLET (LÉON) and A. PORTEVIN. Some Properties of an Industrial Electrolytic Iron	ii, 326
HALA (FRANZ). The Corrosion and Rusting of Iron which has been Treated by the Sherard Process	ii, 326
FALCKE (VICTOR). The Reactions between Ferrous Oxide and Carbon and between Carbon Monoxide and Iron	ii, 327
HENDERSON (WILLIAM E.) and HARRY B. WEISER. Action of Sulphurous Acid on the Sulphides of Iron, Zinc, and Manganese	ii, 327
HAYNES (ELWOOD). Alloys of Cobalt with Chromium and Other Metals	ii, 328
SÉNÉCHAL (A.). The Violet Chromium Sulphates	ii, 328
OLSSON (OSCAR). The Reduction of Tungstic Acid and the Lower Oxidation Stages of Tungsten. I.	ii, 328
RUFF (OTTO) and WALTER MARTIN. The Preparation of Metallic Vanadium	ii, 329
PELABON (HENRI). The System: Antimony Sulphide, Lead Sulphide	ii, 329
KLOOSTER (H. S. VAN). Compounds of Bismuth and Iodine	ii, 330
HOLT (ALFRED), EDWARD C. EDGAR, and JAMES B. FIRTH. The Sorption of Hydrogen by Palladium	ii, 330
LEHMANN (FRANZ). Osmium Dioxide as a Hydrogen Carrier	ii, 331

*Mineralogical Chemistry.*

	PAGE
SPENGLER (ARTHUR COE). Chalcocite Deposition . . . . .	ii, 331
SHADLER (WALDEMAR T.). Homocous Bloodite Crystals . . . . .	ii, 331
KRAMM (H. E.). Serpentes of the Central Coast Ranges of California . . . . .	ii, 331
CORNETIUS (HANS PETER). Petrographical Investigations in the Mountains between the Septimer and Julier Passes . . . . .	ii, 332

*Analytical Chemistry.*

FÉRY (CHARLES) and EUGÈNE TASSILLY. Spectrophotometry in Analysis . . . . .	ii, 332
POZZI-ESCOY (M. EMMANUEL). Vegetable Indicator in Volumetric Analysis . . . . .	ii, 332
WILLIAMS (HERBERT G.). A New Method for the Estimation of Hypochlorites . . . . .	ii, 333
GRABESCHI (IGLIO). Further Observations on the New, Sensitive, and Characteristic Reactions of Bromine. III. . . . .	ii, 333
McMILLAN (R. H.). An Application of the Electric Resistance Furnace to the Estimation of Oxygen in Iron and Steel . . . . .	ii, 333
BOSWELL (MAITLAND C.). Direct Estimation of Oxygen in Organic Compounds . . . . .	ii, 334
MÜLLER (ERICH) and HORST VON FEEBEE. Iodometric Estimation of Persulphuric Acid . . . . .	ii, 334
KOHLER, M. MARQUYROL, and JOVINET. Application of Devarda's Method in the Estimation of Nitrogen in Nitrocelluloses . . . . .	ii, 334
LIPMAN (CHARLES B.) and H. F. PRESLEY. Methods of Estimating Nitrogen in Humus . . . . .	ii, 335
ARTENRIETH (WILHELM) and ALBERT FUNK. Colorimetric Estimations in Water Analysis by means of the Artenrieth-Koenigsberger Colorimeter . . . . .	ii, 335
KRAPIVIN (SERGIUS). Estimation of Ammonia in Effluents and Sewage . . . . .	ii, 335
BONNER (WALTER D.) and EDWIN S. BISHOP. The Rate of Reaction of Nitrous Acid and Carbamide in Dilute Solutions . . . . .	ii, 335
POPP (MAX), J. CONTZEN, H. HOFER, and H. MENZ. Soluble Silicic Acid in Basic Slag and its Effect on the Estimation of the Phosphoric Acid Soluble in Citric Acid . . . . .	ii, 336
WINKLER (LUDWIG W.). The Test for Arsenic with Bettendorf's Reagent . . . . .	ii, 336
MARTY (J.). An Internally Electrically Heated Combustion Tube for Organic Analysis . . . . .	ii, 337
SMITH (H. E.). Gas Bubble and Washing Tube for Combustion Apparatus . . . . .	ii, 337
MILLAR (C. E.). Modification of the Parr Total-carbon Apparatus . . . . .	ii, 337
FRIEDEL (WALTHER). A Method of Examination of Fermentation Gases . . . . .	ii, 337
GATHER (E. W.). A Comparison of Some Qualitative and Quantitative Methods for Carbonates in Soils . . . . .	ii, 338
ROHLAND (PAUL). Estimation of Hardness of Waters . . . . .	ii, 338
WEISSENDERGER (GROERG). Control of the Purification of Boiler Feed Water . . . . .	ii, 338
BOS (J. L. M. VAN DER HORN VAN DEN). Estimation of Potassium by the Cobaltinitrite Method . . . . .	ii, 338
BRADBURY (W. A.) and F. OWEN. Estimation of the Carbonates and Hydroxides of Potassium and Sodium when together in Solution . . . . .	ii, 339
KEISHNAYYA (H. V.). Estimation of Alkalis in Rocks . . . . .	ii, 339
PHANISCHNIKOV (DMITRI N.). Estimation of the Absorbed Bases in Soils . . . . .	ii, 339
HUEY (FREDERIC P.). The Gay-Lussac Method of Silver Estimation . . . . .	ii, 340
IVANOV (V. N.). New Forms of Flask and Beaker for the Volumetric Estimation of Silver, Chlorine, Sulphuric Acid, etc. . . . .	ii, 340
GOOCH (FRANK A.) and D. U. HILL. Purification of Barium Sulphate Precipitated in the Estimation of Barium . . . . .	ii, 340

	Page
IBBOTSON (FREDERICK) and L. AITCHISON. Estimation of Copper in White Metal Alloys	ii, 341
DEMAREST (D. J.). The Thiocyanate Permanganate Method for Copper in Ores	ii, 341
DEMAREST (D. J.). Electrolytic Estimation of Copper in Ores containing Arsenic, Antimony, or Bismuth	ii, 342
TREADWELL (W. D.). The Electro-analytical Separation of Copper from Tungsten and Molybdenum	ii, 342
IVANOV (V. N.). Estimation of Free Acid or Base in Aluminium Sulphate	ii, 343
POZZI-ESCOD (M. EMMANUEL). Rapid Estimation of Manganese in the Presence of Iron	ii, 343
METZGER (FLOYD J.) and L. K. MARRS. The Volumetric Estimation of Manganese in Rock, Slags, Ores, and Spiegels	ii, 344
DITTRICH (MAX). The Estimation of Small Quantities of Manganese and Chromium in Minerals and Rocks	ii, 344
ATACK (FREDERICK W.). Volumetric Estimation of Chromium, Vanadium, and Iron in Presence of One Another	ii, 345
CUSHMAN (ALLERTON S.) and EVERETT B. WETTENGEL. An Electrolytic Method for the Estimation of Tin in Canned Food Products	ii, 346
IBBOTSON (FREDERICK) and L. AITCHISON. Estimation of Tin in Bronzes	ii, 346
FIGHTER (FRITZ) and E. MÜLLER. Volumetric Estimation of Tin by means of Potassium Bromate	ii, 347
PONTO. [Assay of] Alloys of Tin and Antimony	ii, 347
CHESNIAU (GABRIEL). Assay of Commercial Vanadic Acid	ii, 347
WAGENAAR (M.). Relationship of Cesium and Rubidium Salts to the Heavy Metals	ii, 348
MEIMBERG (ENR.) and PAUL WINKER. Separation of Columbium and Tantalum by means of Potassium Chloride in Hydrofluoric Acid Solution	ii, 348
LEBEAU (PAUL) and A. DAMIENS. The Estimation of Acetylenic and Ethylenic Hydrocarbons in Mixtures of Gaseous Hydrocarbons	ii, 349
BARENDRECHT (H. P.). Estimation of Alcohol in Very Dilute Solutions by means of Permanganate	ii, 349
PENCE (C. M.). Potassium Permanganate in the Quantitative Estimation of Some Organic Compounds	ii, 350
LIFSCHITZ (ISAAC). The Quantitative Estimation of the Oxidation Products of Cholesterol	ii, 350
JARNSON-BLOHM (G.). Influence of Ammonium Sulphate in the Polarimetric Estimation of Lactose	ii, 351
LITTELSCHIED (FRANZ M.). Detection of Invert Sugar by means of $\beta$ -Naphthol	ii, 351
ROUSSEAU (EUG.) and MARCELE SIROT. The Soluble Nitrogenous Substances as a Factor for Valuing Flour	ii, 352
HEIDUSCHKA (ALFRED) and A. BERGER. Estimation of Solid Fatty Acids by Heber and Mitchell's Method	ii, 353
TUNMANN (OTTO). Microchemical Analysis of Plants. III. Detection of Chloric Acid, Especially in Resins	ii, 353
NECHAMN (R.). Estimation of Fat in Foods with Special Reference to Extraction with Trichloroethylene	ii, 354
COHN (ROBERT). Lecithin Preparations and the Estimation of Lecithin	ii, 354
VOLLHASE (E.). Detection of Preservatives in Fats (Butter, Margarine, Lard)	ii, 355
OBERMAYER (KENS). Estimation of Commarin in <i>Melilotus vulgaris</i> and <i>officinalis</i>	ii, 355
ROSSET (HENRI). Miscibility Curves for the Estimation of Dissolved Substances: Camphorated Alcohol	ii, 356
REICHARD (C.). Reactions of the Digitalis Glucosides. Digitonin	ii, 356
ROSENTHALER (LEOPOLD). Detection of Saponin	ii, 356

# CONTENTS.

xvii

	PAGE
BRACH (HUGO) and EMIL LENK. Modification of the Liebig Combustion Furnace . . . . .	ii, 530
DEMORFST (D. J.). Estimation of Zinc in Ores . . . . .	ii, 530
LEE (RICHARD EDWIN), ROY H. UHLINGER, and FRANK O. AMON. Method for the Qualitative Analysis of the Zinc Group . . . . .	ii, 530
SMITH (TODD O.) and CHARLES JAMES. Some Quantitative Separations of Neodymium . . . . .	ii, 531
GROFFIER (CHARLES). Detection of Mercury in "Kyanised Wood" . . . . .	ii, 531
JAROS (W.). Precipitation of Aluminium Hydroxide and its Separation from Chromium . . . . .	ii, 531
HYDRICHTS (MAURICE) and N. JOASSART. Estimation of Manganese in Irons and Steels by von Knebe's Process . . . . .	ii, 532
GARRATT (FRANK). Colorimetric Method for the Estimation of Chromium in Steel . . . . .	ii, 532
POZZI ESCUT (M. EMMANUEL). Potassium Iodide and Mercurous Nitrate as a Delicate Reagent for Tungsten and Molybdenum . . . . .	ii, 532
CURMAN (LOUIS J.) and MAX MOSHER. Study of Certain Confirmatory Tests for Tin . . . . .	ii, 532
TERRADWELL (W. D.). The Electrolytic Separation of Tin and Tungsten . . . . .	ii, 533
NISSENSEN (H.). Rapid Methods for the Estimation of Antimony . . . . .	ii, 533
HINRICHSSEN (F. WILLY) and ERICH KINDECHER. The Direct Estimation of Caoutchouc as Tetrabromide . . . . .	ii, 534
VANDEVELDE (ALBERT J. J.). Estimation of Phenols in "Creolines" . . . . .	ii, 534
EGERION (ALFRED C.). The Heat Test . . . . .	ii, 534
HUNTER (WILLIAM H.) and J. D. EDWARDS. Improved Apparatus for the Estimation of Carboxyl Groups in Organic Acids . . . . .	ii, 535
DARIN (HENRY D.), N. W. JANNEY, and ALFRED J. WAREMAN. Estimation of Formic Acid in Urine . . . . .	ii, 536
AGELHON (HENRI). Solubility of Certain Metallic Salts of Volatile Fatty Acids in Organic Solvents. Application to the Qualitative Estimation of these Acids . . . . .	ii, 536
SEIGER (HERMANN). Estimation of Solid Fatty Acids by Hehner and Mitchell's Method . . . . .	ii, 536
ISHIHARA (HIROMI). The Estimation of Lactic Acid in Urine . . . . .	iv, 536
ELLIOTT (THOMAS R.). Estimation of Adrenaline . . . . .	ii, 536

# INDEX OF AUTHORS' NAMES

## IN TRANSACTIONS AND ABSTRACTS

### A.

Abderhalden, E., ii, 457.  
 Abderhalden, E., and A. E. Lampé,  
 i, 671.  
 Agulhon, H., ii, 536.  
 Agulhon, H. See also G. Bertrand.  
 Aktien-Gesellschaft für Anilin-  
 Fabrikation, i, 621.  
 Allan, G. E., and J. Brown, ii, 473.  
 Aloy, J., and C. Rabaut, i, 620.  
 Amadori, M., ii, 512.  
 Ameseder, F. See R. von Zeynek.  
 Amon, F. O. See R. E. Lee.  
 Anderson, E., and H. A. Noyes,  
 ii, 477.  
 Anderson, J. S., ii, 454.  
 André, G., i, 683.  
 Angeli, A., i, 658.  
 Anthes, E. See H. Staudinger.  
 Archibovski, V., i, 687.  
 Arkwright, J. A., i, 683.  
 Armstrong, H. E., and R. T. Colgate,  
 ii, 498.  
 Armstrong, H. E., and C. A. Klein,  
 i, 587.  
 Aron, H., ii, 497.  
 Artmann, P., ii, 528.  
 Askenasy, P., and A. Révai, ii, 472.

### B.

Badische Anilin- & Soda-Fabrik,  
 i, 583.  
 Baeyer, O. von, O. Hahn, and L.  
 Meitner, ii, 109.  
 Bagard, P. See A. Wahl.  
 Bain, (Miss) A. M. See W. H. Mills.  
 Balke, C. W. See J. E. Egan.  
 Baggini, G., i, 628.  
 Bart, H., i, 611.  
 Bartholomaeus, E. See H. Fischer.

Bates, S. J., ii, 466.  
 Baucke, H., ii, 507, 511.  
 Baud, E., i, 586; ii, 475.  
 Bauer, E. See A. Haller.  
 Beck, C. See R. F. Weinland.  
 Beck, O. See J. Troger.  
 Beer, R. See H. Meyer.  
 Benary, E., i, 598.  
 Benary, E., and B. Silbermann,  
 i, 651.  
 Benrath, A., i, 633.  
 Bergeim, O., and P. R. Hawk, i, 608.  
 Bernstein, G., i, 638.  
 Berthelot, D., and H. Gaudechon,  
 ii, 458.  
 Bertiaux, L., ii, 522.  
 Bertrand, G., i, 692.  
 Bertrand, G., and H. Agulhon,  
 i, 692.  
 Beutner, R., ii, 463, 469, 470.  
 Beyerinck, M. W., i, 683.  
 Biddle, H. C., and L. Rosenstein,  
 ii, 492.  
 Bielecki, J., and V. Henri, ii, 455.  
 Biltz, H., and E. Topp, i, 600, 602.  
 Biltz, W., and W. Truthe, i, 593.  
 Bingham, E. O., TRANS., 959.  
 Bloch, M., i, 648.  
 Bottcher, K. A. See S. Gabriel.  
 Bolser, C. E., and L. B. Richardson,  
 i, 605.  
 Bornhardt, C. See W. Schlenk.  
 Bosshard, E., and W. Grob, ii, 525.  
 Bostock, G. D., i, 682.  
 Bosworth, A. W. See L. L. van  
 Slyke.  
 Bouchonnet, A., ii, 497.  
 Bourquelot, E., and E. Verdon,  
 i, 663.  
 Brach, H., and E. Lenk, ii, 530.  
 Bratring, K. See J. Meisenheimer.  
 Braun, J. von, A. Grabowski, and  
 G. Kirschbaum, i, 612.  
 Brauns, R., and J. Uhlig, ii, 519.

Brenck, H., ii, 514.  
 Brewster, C. M. See H. A. Torrey.  
 Brézina, E. See O. Togel.  
 Bridel, M., i, 690.  
 Briggs, G. J., i, 594.  
 Briggs, T. R., ii, 506.  
 Brillouin, M., ii, 493.  
 Broek, A. van der, ii, 460.  
 Brown, A. R., ii, 454.  
 Brown, J. See G. E. Allan.  
 Bruni, G., and G. Scarpa, ii, 472.  
 Bruylants, P., and A. Byteler, ii, 500.  
 Bub, J. See G. Heller.  
 Buglia, G., and A. Costantino, i, 676.  
 Burge, W. E., i, 662.  
 Burgstaller, A. See V. Rothmund.  
 Buswell, H. L. F., i, 665.  
 Byteler, A. See P. Bruylants.

C.

Cain, J. C., J. L. Simonsen, and C. Smith, TRANS., 1035.  
 Cambi, L., i, 606.  
 Cannon, W. B., and L. B. Nice, i, 677.  
 Charpy, G., and A. Cornu, ii, 512.  
 Chauvenet, E., ii, 514.  
 Chauvenet, E., and G. Urbain, ii, 479.  
 Chernoff, L. H. See T. B. Johnson.  
 Ciani, R., and R. Luzzatto, i, 631.  
 Clark, A. J., i, 674.  
 Claude, G., ii, 503.  
 Clausmann, P. See A. Gantier.  
 Coade, (Miss) M. E., and E. A. Werner, TRANS., 1221.  
 Cohen, E., ii, 514.  
 Cohnheim, O., i, 672, 679.  
 Colgate, R. T. See H. E. Armstrong.  
 Colman, J. See S. Gabriel.  
 Cornu, E., ii, 466.  
 Cornu, A. See G. Charpy.  
 Costantino, A. See G. Buglia.  
 Coste, J. H., ii, 474.  
 Courtman, H. B. See T. M. Lowry.  
 Courtois, G., i, 585.  
 Cranston, J. A., ii, 464.  
 Crommelin, C. A. See E. Mathias, and H. K. Onnes.  
 Crossley, A. W., and W. R. Pratt, TRANS., 982.  
 Crossley, A. W., and S. Smith, TRANS., 969.  
 Collis, (Miss) W. C., and (Mrs.) E. M. Tibb, i, 673.  
 Cumming, A. C. See T. M. Finlay.

Curtman, L. J., and M. Mosher, ii, 532.  
 Cusmano, G., i, 606.

D.

Dakin, H. D., i, 671.  
 Dakin, H. D., and H. W. Dudley, i, 665.  
 Dakin, H. D., N. W. Janney, and A. J. Wakeman, i, 679.  
 Dale, (Miss) D. i, 680.  
 Dale, H. H., i, 675.  
 Dalström, Y., i, 592.  
 Dean, E. W. See W. A. Drushel.  
 Delattre, G., ii, 527.  
 Demorest, D. J., ii, 536.  
 Denis, W. See G. G. Scott.  
 Deventer, C. M. van, ii, 472.  
 Dewey, L. H. See J. H. Mathews.  
 Dickson, T. W. See T. M. Lowry.  
 Diemer, M. E., ii, 515.  
 Dienert, F., ii, 504.  
 Dillon, T. See H. Ryan.  
 Dima, G. A., ii, 465.  
 Dixon, A. E., and J. Taylor, TRANS., 974.  
 Dobbie, J. J., and J. J. Fox, TRANS., 1193.  
 Dodonow, J. See J. Meisenheimer.  
 Dolezalek, F., ii, 481.  
 Dolezalek, F., and A. Schulze, ii, 482.  
 Doriencourt, H., i, 651.  
 Drushel, W. A., and E. W. Dean, ii, 491.  
 Dudley, H. W. See H. D. Dakin.  
 Dunlop, J. G. M., i, 591.  
 Dunstan, A. E. See F. B. Thole.  
 Durig, A. See O. Togel.  
 Dvořák, J., i, 691.

E.

Eckert, F., ii, 465.  
 Edwards, J. D. See W. H. Hunter.  
 Efremov, N. N., i, 635.  
 Egan, J. R., and C. W. Balke, ii, 508.  
 Egerer, W. See K. Scholl.  
 Egerton, A. C., ii, 534.  
 Ehrenreich, K. See C. Seer.  
 Ehrhardt, U. See K. A. Hofmann.  
 Ekeley, J. R., i, 682.  
 Elliott, T. R., i, 671.  
 Elsdon, A. V., and J. F. Stansfield, TRANS., 1039.  
 Endle, E. See H. Staudinger.  
 Ennos, F. R., ii, 491.  
 Ephraim, F., ii, 496.



Krpf-Lefkowiez, T. A. See J. Rosen-  
bloom.  
Encken, A., ii, 474.

## F.

Fajans, K., ii, 493.  
Fulk, K. G., i, 604.  
Farbenfabriken vorm. F. Bayer  
& Co., i, 611, 647.  
Farbwerk Mühlheim vorm. A. Leon-  
hardt & Co., i, 648.  
Farbwerke vorm. Meister, Lucius,  
& Brüning, i, 633, 634.  
Feinberg, M., i, 643.  
Fenger, F., i, 676.  
Fenigen, R., i, 680.  
Findlay, A., and G. King, TRANS.,  
1170.  
Finlay, T. M., and A. C. Cunningham  
TRANS., 1004.  
Fischer, A., and L. Michiels, i, 584.  
Fischer, A., E. K. Rideal, and A.  
Roderburg, ii, 513.  
Fischer, H., E. Bartholomäus, and  
H. Röse, i, 660.  
Fischer, H., and A. Hahn, i, 613.  
Fleck, A., TRANS., 1052; ii, 464.  
Fletcher, A. L., ii, 516, 521.  
Foreaud, R. de, ii, 477.  
Foster, M. L., i, 684.  
Fox, J. J., and F. G. Pope, TRANS.,  
1263.  
Fox, J. J. See also J. J. Dobbie.  
Fraenkel, W., ii, 509.  
Francesconi, L., and E. Sernagiotto,  
i, 636.  
Frank, A., i, 674.  
Frankland, E. P., and H. E. Smith,  
TRANS., 898.  
Fresenius, R., ii, 522.  
Freundlich, H. See N. Ishizaka.  
Friederici, K. See A. Stock.  
Friedrichs, F., ii, 497.  
Friese, W., ii, 498.

## G.

Gabriel, S., K. A. Bottcher, and J.  
Colman, i, 622.  
Gadamer, J., and M. Kuntze, i, 621.  
Garratt, F., ii, 532.  
Gaubert, P., i, 643.  
Gaudechon, H. See D. Berthelot.  
Gautier, A., and P. Clausmann,  
i, 677.  
Gibson, G. E., ii, 478.  
Glagolev, P., i, 670.  
Glaser, F., ii, 465.  
G.

Glenny, A. T., i, 680.  
Gluud, W., TRANS., 1251.  
Goerens, P., and G. Hartel, ii, 511.  
Goldschmiedt, G., i, 643.  
Gomberg, M., and R. L. Jickling,  
i, 641.  
Gortner, R. A., i, 673.  
Grabowski, A. See J. von Braun.  
Greaves, J. E. See R. Stewart.  
Greenwald, I., i, 667, 670.  
Griesbach, W., i, 667.  
Grob, W. See E. Rosshard.  
Groffier, C., ii, 531.  
Grünberg, K., ii, 516.  
Grünling, F., ii, 516.  
Guérin, G., i, 642.  
Guthier, A., and E. Sauer, ii, 505.  
Guyot, A., and A. Kovache, i, 647.

## H.

Haar, A. W. van der, i, 640.  
Habermann, J., ii, 490.  
Hackspill, L., ii, 503.  
Hämäläinen, J., i, 635, 639.  
Hageman, A. M. See H. B. North.  
Hahn, A. See H. Fischer.  
Hahn, O., and M. Rothenbach,  
ii, 463.  
Hahn, O. See also O. von Baeyer.  
Haller, A., i, 629.  
Haller, A., and E. Bauer, i, 591.  
Halsall, R. See G. Owen.  
Hamlin, M. L., i, 665.  
Hanriot, M., and A. Kling, i, 593.  
Hardy, W. B., ii, 489.  
Hartel, G. See P. Goerens.  
Hartley, E. G. J., TRANS., 1196.  
Hasselblatt, M., ii, 484.  
Hawk, P. B. See O. Bergeim.  
Haworth, W. N., TRANS., 1242.  
Haworth, W. N., W. H. Perkin,  
jun., and O. Wallach, TRANS., 1225.  
Heard, W. N., i, 658.  
Heike, W., ii, 477.  
Heinemann, F., i, 697.  
Heller, C., and L. Bob, i, 631.  
Henderson, W. E., and D. R. Kellogg,  
ii, 492.  
Henri, V. See J. Bielecki.  
Heuser, E. See R. Scholl.  
Heymann, P. See R. Stoermer.  
Hildebrand, J. H., ii, 470.  
Hill, (Miss) A. M. See A. V. Hill.  
Hill, A. V., and (Miss) A. M. Hill,  
i, 666.  
Hinrichsen, F. W., and R. Kempf,  
i, 637.  
Hinrichsen, F. W., and E. Kins-  
scher, i, 639; ii, 534.

Hinrichsen, F. W., H. Quensell, and E. Kindscher, i, 637.  
 Hober, R., and O. Nast, ii, 486.  
 Hof, H., ii, 506.  
 Hofmann, K. A., and U. Ehrhardt, i, 599.  
 Hogan, A. G. See C. O. Johns.  
 Holden, H. C. See C. James.  
 Holdermann, K. See R. Scholl.  
 Holm, H., ii, 478.  
 Holzberg, H. L., i, 662.  
 Homer, (Miss) A., i, 646.  
 Howden, R., ii, 522.  
 Huguenot, L., and A. Morel, i, 665.  
 Hunter, W. H., and J. D. Edwards, ii, 535.  
 Huybrechts, M., and N. Joassart, ii, 532.

## I.

Ishihara, H., ii, 536.  
 Ishizaka, N., and H. Freundlich, ii, 486.

## J.

Jacobi, C., i, 680.  
 Jakob, W., ii, 531.  
 James, C., and H. C. Holden, ii, 503.  
 James, C. See also T. O. Smith.  
 Jauney, N. W. See H. D. Dakin.  
 Javillier, M., i, 692.  
 Jickling, R. L. See M. Gomborg.  
 Joassart, N. See M. Huybrechts.  
 Johns, C. O., and A. G. Hogan, i, 657.  
 Johnson, C. M., ii, 524, 529.  
 Johnson, T. B., i, 587.  
 Johnson, T. B., and L. H. Chernoff, i, 658.  
 Johnson, T. B., R. C. Moran, and E. F. Kohmann, i, 611.  
 Jones, B. M., and F. G. Shah, TRANS., 1043.  
 Joubiaux, A. See P. Pascal.

## K.

Karandev, V. V., ii, 518.  
 Kauffmann, H., ii, 493.  
 Kauffmann, W., ii, 462.  
 Kaye, G. W. C., ii, 465.  
 Keegan, P. Q., i, 689.  
 Keller, O., and O. Völker, i, 642.  
 Kellogg, D. K. See W. E. Henderson.  
 Kempf, R. See F. W. Hinrichsen.  
 Keyes, F. G. See G. N. Lewis.

Kindscher, E. See F. W. Hinrichsen.  
 King, G. See A. Findlay.  
 Kirschbaum, G. See J. von Braun.  
 Klason, P., and H. Mellquist, ii, 526.  
 Kleeman, R. D., ii, 479.  
 Klein, C. A. See H. E. Armstrong.  
 Kling, A. See M. Hanriot.  
 Knoll & Co., i, 661.  
 Knudson, L., i, 637.  
 Koch, (Miss) M. L., i, 673.  
 Koch, (Miss) M. L. See also W. Koch.  
 Koch, W., and (Miss) M. L. Koch, i, 673.  
 Kohmann, E. F. See T. B. Johnson.  
 Kohnstamm, P., and J. Timmermans, ii, 481.  
 Kossel, A., i, 672.  
 Kostytschev, S., i, 688.  
 Kovache, A. See A. Guyot.  
 Krauss, E., i, 680.  
 Krauss, L. See E. Schmidt.  
 Kriebler, V. K., i, 663.  
 Kuligren, C., ii, 525.  
 Kuncell, F., and K. Puls, i, 611.  
 Kuntze, M. See J. Gadamer.

## L.

Laar, J. J. van, ii, 471, 472.  
 Lafon, G., i, 677.  
 Lambris, G., ii, 523.  
 Lampé, A. E. See E. Abderhalden.  
 Landau, S., and H. Piwnikiewicz, ii, 462.  
 Landolph, F., i, 650.  
 Landsberg, M., i, 663.  
 Landsteiner, K., i, 668.  
 Langer, A. See R. Scholl.  
 Lautenot, M., i, 583.  
 Lapworth, A., TRANS., 1029.  
 Leathes, J. W., i, 691.  
 Lebedev, A. von, i, 592, 634.  
 Lederer, K., i, 615.  
 Ledue, A., ii, 474.  
 Lee, R. E., R. H. Uhlinger, and F. O. Amon, ii, 530.  
 Leetham, (Miss) C., i, 674.  
 Lehmann, E., i, 667.  
 Leighton, A., ii, 459.  
 Lenher, V., ii, 514.  
 Lenk, E. See H. Brach.  
 Lepierre, C., i, 686.  
 Le Sueur, H. R., TRANS., 1119.  
 Leven, P. A., and C. J. West, i, 587.  
 Levy, P., i, 620.

- Lewis, G. N., and F. G. Keyes, ii, 467.  
 Lewis, H. B., i, 671.  
 Lichtwitz, L., i, 657.  
 Liebig, H. von, i, 607.  
 Liesegang, R. E., ii, 453.  
 Linhart, G. A., ii, 490.  
 Lipman, C. B., i, 692.  
 Lloyd, S. J., ii, 466.  
 Loeb, A., i, 667.  
 Loeb, J., and H. Wasteneys, i, 672.  
 Lombroso, U., i, 664.  
 Loring, F. H., ii, 493.  
 Lowry, T. M., TRANS., 1062.  
 Lowry, T. M., and H. B. Courtman, TRANS., 1214.  
 Lowry, T. M., and T. W. Dickson, TRANS., 1067.  
 Lundberg, J., i, 685.  
 Lunnon, R. G., ii, 475.  
 Luzzatto, R. See R. Ciusa.  
 Lvov, S., i, 686.  
 Lvov, S. D. See V. I. Palladin.

## M.

- Maass, O., and D. McIntosh, i, 584.  
 McClelland, N. P. See J. E. Purvis.  
 McClenahan, F. M., i, 690.  
 McIntosh, D. See O. Maass.  
 McLennan, J. C., ii, 455.  
 Madsen, E. H., TRANS., 965.  
 Maillard, L. C., i, 685.  
 Malfitano, G., and (Mlle.) A. N. Moschkov, i, 593.  
 Mallison, H. See H. Stobbe.  
 Manchot, W., i, 667.  
 Marcille, R., 685.  
 Marcusson, J., i, 581.  
 Marcusson, J., and C. Vieltitz, i, 581.  
 Masson, I., ii, 483.  
 Masters, (Miss) H., and H. L. Smith, TRANS., 992.  
 Mathews, A. P., i, 582; ii, 494, 495, 496.  
 Mathews, J. H., and L. H. Dewey, ii, 459, 461.  
 Mathias, E., H. K. Onnes, and C. A. Crommelin, ii, 473.  
 Matignon, C., ii, 504, 505.  
 Mantlner, F., i, 629, 632.  
 Mayer, P., i, 667, 686.  
 Mecklenburg, W., ii, 529.  
 Meillere, G., ii, 529.  
 Meisenheimer, J., K. Bratring, and J. Dodonow, i, 595.  
 Meitner, L. See O. von Baeyer.  
 Mellanby, J., and V. G. Woolley, i, 662.  
 Mellquist, H. See P. Klason.

- Mendel, L. B. See T. B. Osborne.  
 Merck, E., i, 656.  
 Merrill, G. P., ii, 520.  
 Meyer, H., and R. Beer, i, 617.  
 Meyer, H., and K. Schlegel, i, 608.  
 Meyer, J., i, 583.  
 Michel, H., ii, 518.  
 Michiels, L. See A. Fischer.  
 Milbauer, J., i, 595.  
 Mills, W. H., and (Miss) A. M. Bain, i, 651.  
 Milner, S. R., ii, 481.  
 Moore, R. B., ii, 465.  
 Moore, W. C., ii, 467.  
 Moran, R. C. See T. B. Johnson.  
 Morel, A. See L. Hugouenq.  
 Moschkov, (Mlle.) A. N. See G. Malfitano.  
 Mosher, M. See L. J. Curtman.  
 Morcho, V., i, 678.  
 Müller, E., ii, 526.  
 Mussell, A. G. See F. B. Thole.

## N.

- Nast, O. See R. Hüber.  
 Natus, B., ii, 527.  
 Naunton, W. J. S. See F. Tutin.  
 Neubert, J. K., ii, 510.  
 Neumann, S., ii, 457.  
 Nice, L. B. See W. B. Cannon.  
 Nissenon, H., ii, 533.  
 North, H. B., and A. M. Hageman, ii, 499, 506.  
 Norzi, G. See C. Porlezza.  
 Noyes, H. A. See E. Anderson.

## O.

- Oberhoffer, P., ii, 511.  
 Obermayer, F., and R. Willheim, i, 668.  
 Oden, S., ii, 455.  
 O'Donoghue, C. H., i, 675.  
 Oehsner de Coninck, W., i, 689; ii, 504.  
 Oehme, C., i, 681.  
 Oehme, H. See C. Paal, and A. Sieverts.  
 Oertel, R., i, 591.  
 Onnes, H. K., and C. A. Crommelin, ii, 474.  
 Onnes, H. K., and E. Oosterhuis, ii, 473.  
 Onnes, H. K. See also E. Mathias.  
 Oosterhuis, E. See H. K. Onnes.  
 Osborne, T. B., and L. B. Mendel, i, 690.  
 Osterwalder, A., i, 683.  
 Owen, G., and R. Halsall, ii, 463.

P.

- Paal, C., and H. Oehme, i, 534.  
 Paladino, R., i, 675.  
 Palladin, V. I., and S. D. Lvov, i, 684.  
 Panzer, T., i, 662.  
 Parker, E. G., i, 594.  
 Pascual, P., and A. Jouniaux, ii, 509.  
 Pauli, W. E., ii, 456.  
 Piddle, C. J., and W. E. S. Turner, TRANS, 1202.  
 Penfeld, W. J., i, 684.  
 Perkin, W. H., jun. See W. N. Haworth.  
 Philippi, E., i, 627.  
 Philippi, E., and A. Uhl, i, 598.  
 Piccard, A., ii, 473.  
 Piettre, M., and A. Vila, i, 661.  
 Pilcher, J. D., i, 679.  
 Pienikiewicz, H. See S. Landau.  
 Pope, F. G., and (Miss) W. I. Willett, TRANS, 1258.  
 Pope, F. G. See also J. J. Fox.  
 Pope, W. J., and J. Read, i, 646.  
 Popov, S. P., ii, 517.  
 Portezza, C., and G. Norzi, ii, 498.  
 Portevin, A., ii, 479.  
 Pozzi Escot, M. E., ii, 524, 526, 532.  
 Piatolongo, U., ii, 467.  
 Pratt, W. R. See A. W. Crossley.  
 Puls, K. See F. Kunczell.  
 Purvis, J. E., and N. P. McClelland, TRANS, 1088.

Q.

- Quensell, H. See F. W. Hinrichsen.

R.

- Rabaut, C. See J. Aloy.  
 Rakoczy, A., i, 669.  
 Ran, O., ii, 523.  
 Rakshit, J. N., i, 606.  
 Ray, B. J. See W. A. Withers.  
 Read, J. See W. J. Pope.  
 Reboal, G., ii, 489.  
 Reichinstein, D., ii, 468.  
 Reissert, A., i, 621.  
 Rempy, F. G. P., TRANS, 1076.  
 Ryan, C. See A. Windaus.  
 Ryan, A. See P. Askenasy.  
 Rhoad, T. F. E., and K. V. Wheeler, TRANS, 1210.  
 Richards, T. W., ii, 483.  
 Richardson, H. See E. Rutherford.  
 Richardson, L. B. See C. E. Bolser.  
 Riedel, E. K. See A. Fischer.  
 Ritz, L., ii, 468.

- Ringer, A. I. See A. E. Taylor.  
 Robert, (Mlle.) C., i, 680.  
 Robertson, T. B., ii, 492.  
 Roderburg, A., ii, 513.  
 Roderburg, A. See also A. Fischer.  
 Röse, H. See H. Fischer.  
 Rose, W. C. See A. E. Taylor.  
 Rosenbloom, J., i, 673, 676, 679, 687.  
 Rosenbloom, J., and T. A. Erpf-Lefkovicz, i, 675.  
 Rosenatein, L. See H. C. Biddle.  
 Rosenthaler, L., i, 663.  
 Rosenbach, M. See O. Hahn.  
 Rothmund, V., and A. Burgstaller, ii, 489, 524.  
 Rutherford, E., and H. Richardson, ii, 461.  
 Ruttan, R. F., i, 586.  
 Ryan, H., and T. Dillon, i, 583.

S.

- Saccharin-Fabrik Aktiengesellschaft vorm. Fahlberg, List & Co., i, 611.  
 Salway, A. H., TRANS, 1022.  
 Sauer, E. See A. Gutbier.  
 Scaffidi, V., i, 676.  
 Scarpa, G. See G. Bruni.  
 Scharvin, W. W., i, 661.  
 Schlegl, K. See H. Meyer.  
 Schleicher, A., ii, 497.  
 Schlenk, W., i, 610.  
 Schlenk, W., and C. Bornhardt, i, 610.  
 Schmidt, E., L. Krauss, and A. Seeburg, i, 643.  
 Schmidt, J., and A. Sigwart, i, 651.  
 Scholl, R., i, 611.  
 Scholl, R., W. Egerer and E. Heuser, i, 583.  
 Scholl, R., K. Holdermann, and A. Langer, i, 598.  
 Schreinemakers, F. A. H., ii, 439.  
 Schulov, I., i, 688.  
 Schulze, A. See F. Dolezalek.  
 Schumoff-Deleano, V., ii, 517.  
 Schweser, F., ii, 433.  
 Scott, G. G., and W. Denis, i, 673.  
 Seeburg, A. See E. Schmidt.  
 Seer, C., i, 633.  
 Seer, C., and K. Ehrenreich, i, 634.  
 Segaller, D., TRANS, 1154.  
 Serger, H., ii, 536.  
 Sernagiotto, E. See L. Francesconi.  
 Shah, P. G. See B. M. Jones.  
 Shipsey, (Miss) K., and E. A. Werner, TRANS, 1255.  
 Sieburg, R., i, 639, 640.

Siegfried, M., i, 662.  
 Siertsema, L. H., ii, 453.  
 Sieverts, A., and H. Oehme, ii, 476.  
 Siggel, A., ii, 477.  
 Sigwart, A. See J. Schmidt.  
 Silbermann, R. See E. Benary.  
 Simon, A. L., ii, 505.  
 Simonsen, J. L., TRANS., 1144.  
 Simonsen, J. L. See also J. C. Cain.  
 Sirks, J. F., ii, 438.  
 Skinner, J. J., i, 691.  
 Slater, A., ii, 491.  
 Slyke, L. L. van, and A. W. Bosworth, i, 659, 680.  
 Smith, C. See J. C. Cain.  
 Smith, H. E. See E. P. Frankland.  
 Smith, H. L. See (Miss) H. Masters.  
 Smith, S. See A. W. Crossley.  
 Smith, T. O., and C. James, ii, 531.  
 Smits, A., ii, 499.  
 Splittgerber, A. See J. Tillmans.  
 Stadeler, A., ii, 512.  
 Stanek, V., i, 659.  
 Stansbie, J., ii, 591.  
 Stausfield, J. F. See A. V. Eidsen.  
 Stark, J., ii, 456.  
 Staudinger, H., and E. Anthes, i, 604, 616.  
 Staudinger, H., and R. Endle, i, 592.  
 Stepp, W., i, 670.  
 Stewart, R., and J. E. Greaves, ii, 528.  
 Stobbe, H., and H. Mallison, ii, 459.  
 Stock, A., and K. Friederici, ii, 502.  
 Stoermer, R., and P. Heymann, i, 618.  
 Stremme, H., ii, 519.

## T.

Tarugi, N., ii, 510.  
 Taylor, A. E., and A. I. Ringer, i, 672.  
 Taylor, A. E., and W. C. Rose, i, 672.  
 Taylor, J. See A. E. Dixon.  
 Thirring, H., ii, 471.  
 Thole, F. R., A. G. Russell, and A. E. Dunstan, TRANS., 1105.  
 Thomae, C., i, 688.  
 Thomas, P., ii, 527.  
 Thomsen, E., i, 669.  
 Thomson, (Sir) J. J., ii, 502.  
 Tillmans, J., and A. Splittgerber, ii, 528.  
 Timmermans, J. See P. Kohnstamm.  
 Titov, V. S., ii, 480.

Togel, O., E. Brozina, and A. Durig, i, 670.  
 Tolman, R. C., ii, 488.  
 Topp, E. See H. Biltz.  
 Torrey, H. A., and C. M. Brewster, i, 649.  
 Towtkiewicz, W. See T. Wajnski.  
 Treadwell, W. D., ii, 533.  
 Triba, (Mrs.) E. M. See (Miss) W. C. Cullis.  
 Tröger, J., and O. Beck, i, 630.  
 Trnthe, W. See W. Biltz.  
 Tschernik, G. P., ii, 518.  
 Turner, W. E. S. See C. J. Peddle.  
 Tutin, F., and W. J. S. Naunton, i, 639.

## U.

Uhl, A. See E. Philippi.  
 Uhl, K., i, 659.  
 Uhlig, J. See R. Brannus.  
 Uhlinger, R. H. See R. E. Lee.  
 Urbain, G. See E. Chauvenet.  
 Uspenski, A. E. See N. D. Zelinski.

## V.

Vandeveldt, A. J. J., ii, 534.  
 Verdon, E. See E. Bourquelot.  
 Viale, G., i, 676.  
 Vietlitz, C. See J. Marcusson.  
 Vigouroux, E., ii, 512.  
 Vila, A. See M. Piettra.  
 Völker, O. See O. Keller.  
 Voisenet, E., i, 685, 686.  
 Volmer, M., ii, 456.  
 Voswinkel, H., ii, 498.

## W.

Waddell, J., ii, 522.  
 Wahl, A., and P. Bagard, i, 654.  
 Wakeman, A. J. See H. D. Dakin.  
 Walburn, L. E., ii, 522.  
 Walker, J., TRANS., 1227.  
 Wallach, O. See W. N. Haworth.  
 Warynski, T., and W. Towtkiewicz, ii, 514.  
 Wasteneys, H. See J. Loeb.  
 Wedekind & Co., R., i, 634.  
 Weinland, K. F., and C. Beck, i, 64.  
 Weisspfenning, G. See T. Zinck.  
 Werner, E. A., TRANS., 1010.  
 Werner, E. A. See also (Miss) M. E. Coade and (Miss) K. Shipsey.  
 West, C. J. See P. A. Levene.  
 Westgren, A., ii, 485.

- |   |  |
|---|--|
| Wheeler, L. P., ii, 453.<br>Wheeler, R. V. See T. F. E. Rhend.<br>Whitby, G. S., i, 636.<br>Wiegner, G., 691.<br>Willett, (Miss) W. I. See F. G. Pope.<br>Wilhelm, R. See F. Obermayer.<br>Windaus, A., and C. Resau, i, 615.<br>Winkler, L. W., ii, 527.<br>Winther, C., ii, 458.<br>Withers, W. A., and B. J. Ray,<br>i, 691.<br>Wladyczko, S., i, 682. | Wolff, A., i, 615.<br>Woolley, V. J. See J. Mellanby.<br><br><p style="text-align: center;">Z.</p> Zelinski, N. D., and A. E. Uspenski,<br>i, 607.<br>Zeynek, R. von, and F. Ameseder,<br>i, 678.<br>Zincke, T., and G. Weisspenning,<br>i, 655. |
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## ERRATA.

## VOL. CHL (TRANS., 1913).

- | Page | Line   |
|------|--|
| 617  | 16—17 for "whence $[\alpha]_D + 7.21^\circ$ and $[M]_D + 22.9^\circ$ " <i>read</i><br>" CH " "whence $[\alpha]_D + 3.72^\circ$ and $[M]_D + 11.8^\circ$ ." |
| 947  | in formula II for $\diagup \text{CH}_2 \text{ read } \diagup \text{CH}_2$  |



## Organic Chemistry.

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**Notes on Mine Gas Problems.** GEORGE A. BURRELL (*J. Ind. Eng. Chem.*, 1913, 5, 181—186).—The author gives an account of the various problems met with in connexion with mine gases, interpolating from time to time some of the data accumulated by the Bureau of Mines with respect to the explosibility and physiological effects of mine atmospheres, and to flame extinction and after-damp.

The lower explosive limit of mixtures of air and methane is confirmed to be 5.5% methane. The presence of carbon dioxide alters this explosive limit, but even 10% of carbon dioxide raises it only to 6.6%. Reduction in the volume percentage of oxygen also raises the explosive limit. Harger has suggested that a small reduction in the oxygen percentage and a small increase in the carbon dioxide percentage in mine air will suffice to produce an atmosphere incapable of supporting combustion, and consequently an atmosphere in which explosions and gob fires cannot occur, but the data obtained by the Bureau of Mines indicate that the figures given by Harger are much too low, both with respect to the increase in carbon dioxide and diminution in oxygen.

When acetylene is used in the miner's lamp, the flame resembles the ordinary wick flame burning in pure air, when the oxygen content of the air decreases to 16—16.5%; this behaviour of the flame can be used as a guide to men venturing into workings containing black damp and less oxygen than the percentage given. The ordinary miner's lamp is extinguished when the oxygen falls to about 16.5—17%; the extinguishing of the flame is shown to be due to deficiency in oxygen and not to the presence of carbon dioxide.

Reference is made to the following subjects: Effect of vitiated air on the luminosity of miner's lamps (compare Haldane, *Colliery Guardian*, Oct. 23th, 1912); high velocity of air currents in mines; distribution of after-damp; intrusion of natural gas into mines, etc. Analyses are also given of mine-gas mixtures containing explosive and other proportions of methane, and of samples of after-damp atmospheres which show the large amount of carbon monoxide (white-damp) present shortly after an explosion.

T. S. P.

**Solvents for Acetylene.** JOSEPH H. JAMES (*J. Ind. Eng. Chem.*, 1913, 5, 115—120).—An investigation of the solvent powers for acetylene of a number of organic liquids shows that those containing the carbonyl group are generally the best solvents. Organic acids must be excluded, however, the hydroxyl in the carboxyl group seeming to inhibit the solvent action of the carbonyl. The presence of the carbonyl group is not sufficient, of itself, to account for the solubility, since methylal and acetal are very good solvents.

It is found that acetaldehyde fulfils all the industrial requirements for an acetylene solvent.

T. S. P.



**Preparation of Dimethylacetylene [Crotonylene] and Ethylacetylene from Carbides.** CARL WILH. SCHLICHTER (D.R.P. 253802).—When methyl alcohol is heated with an alkaline earth carbide during four days at 60–120° under a pressure of 50 atmospheres, or during six days in a closed tube at 200° it yields a mixture of crotonylene ( $\Delta^2$ -butinene),  $\text{CMe:CHMe}$ , b. p. 28°, and ethylacetylene [ $\Delta^2$ -butinene],  $\text{CEt:CH}$ , b. p. 18°. F. M. G. M.

**$\Delta^2$ -Heptatriene and Related Substances.** CORNELIS J. ENKLAAR (*Chem. Weekblad*, 1913, 10, 187–189. Compare this vol., i, 243).—A discussion of the influence of structure on the possibility of solidifying unsaturated hydrocarbons. By cooling with liquid air several butadienes and related substances have been converted into the solid state. A. J. W.

**Vinylacetylene.** RICHARD WILLSTÄTTER and THEODOR WIRTH (*Ber.*, 1913, 46, 535–538).—By the action of dimethylamine in benzene solution on the dibromide of butadiene,  $\alpha\delta$ -tetramethyl diamino- $\Delta^2$ -butylene,  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH:CH}\cdot\text{CH}_2\cdot\text{NMe}_2$ , is obtained. The use of an indifferent solvent, such as benzene, is essential; with alcohol numerous secondary reactions take place.

When the corresponding quaternary ammonium base is distilled in a vacuum it is decomposed, and vinylacetylene,  $\text{CH}_2\text{C:CH:CH}_2$ , is obtained.

$\alpha\delta$ -Tetramethyldiaminobutylene is a colourless oil with a narcotic odour, b. p. 171–172°/723 mm., 65–65.5°/17 mm.,  $D_4^{20}$  0.8198. The *picrate* forms needles, m. p. 222–223°; the *aurichloride* separates in crystalline needles, m. p. 201° (decomp.); the *platinichloride*,  $2\text{H}_2\text{O}$ , crystallises in long, rhombic prisms, m. p. 227–228°, whilst the *dimethiodide* forms prisms, decomp. 270°.

Vinylacetylene [ $\Delta^2$ -butenylene] melts to a colourless liquid, b. p. 2–3°/729 mm., and has an odour like acetylene. It forms a greenish-yellow copper salt and a colourless, crystalline silver salt, which explodes when heated. E. F. A.

**A Catalytic Method of Isomerisation of Alkyl Chlorides and Bromides.** PAUL SAEATIER and ALPHONSE MAILHE (*Compt. rend.*, 1913, 156, 658–659. Compare A., 1905, i, 677).—Barium chloride or thorium chloride at 250° causes the decomposition of primary alkyl chlorides or bromides into ethylene hydrocarbons and hydrogen chloride or bromide. These then recombine, when passed over pumice stone at 200°, giving, not the original haloid, but the isomeric chloride or bromide. The resulting liquid is submitted to fractional distillation, thus separating any of the original unchanged substance. W. G.

**Trichloroethylene and Some of its Derivatives.** JACOB BOESEKEN [with C. E. KLAMER and J. G. DE VOOET] (*Rec. trav. chim.*, 1913, 32, 15–22).—Unsuccessful attempts have been made to bring trichloroethylene and tetrachloroethylene into reaction with benzoyl chloride, sulphur chloride, phosphorus chloride, thionyl chloride, and

sulphuryl chloride respectively in the presence of aluminium chloride. Charred products were obtained, except in the case of tetrachloroethylene and sulphuryl chloride, when hexachloroethane was isolated, owing to the decomposition of sulphuryl chloride into sulphur dioxide and chlorine and union of the latter with tetrachloroethylene.

Barium monochlorosulphoacetate,  $C_2H_3O_3ClSbA$ , was isolated from the product of the action of fuming sulphuric acid (containing 10%  $SO_3$ ) on trichloroethylene at 88°.

When trichloroethylene was added drop by drop to a mixture of nitric acid (D 1.5) and concentrated sulphuric acid, cooled by a freezing mixture of salt and ice, and the action interrupted as soon as the temperature of the product rose but slowly when removed from the freezing mixture, dichloroacetic acid was obtained, together with a substance,  $\text{C}_2\text{H}_3\text{N}_2\text{Cl}_3$ , b. p.  $32^\circ/36$  mm., which, when preserved, became converted into colourless, very hygroscopic needles, which were insoluble in, or decomposed by, the ordinary solvents, and had mol. wt. 194 in nitrobenzene solution. When heated with hydrochloric acid, this substance yielded small amounts of nitric oxide and carbon dioxide, but neither hydroxylamine nor oxalic acid could be

detected. Alcoholic potassium hydroxide decomposed it according to the equation:  $C_2H_2O_2N_2Cl_3 + 7KOH = 3KCl + 2K_2CO_3 + 4H_2O + N_2$ . With zinc and cold dilute sulphuric acid it gave a quantitative yield of ammonia. It did not give Liebermann's reaction. In

view of the above properties, the annexed formula is tentatively proposed for it.

**Elimination of Water from Pinacolyl Alcohol. Tertiary Butylethylene.** W. FOXIN and N. SOCHANSKI (*Ber.*, 1913, 46, 244-248).—Pinacolyl alcohol was converted by Couturier (*A.*, 1893, i, 245) into a bromide, which, when treated with solid potassium hydroxide, gave a mixture of  $\beta$ -dimethyl- $\Delta^2$ -butylene (compare Zelinsky and Zelikov, *A.*, 1902, i, 2) with a small quantity of a hydrocarbon, b. p. 56-59°, which was described as *tert.*-butyl ethylene. The latter compound has now been prepared from pinacolyl alcohol by Tschugaev's method and has other properties.

The potassium derivative is prepared by adding the alcohol to potassium *tert*-amyloxide (compare Tschugaev, A., 1905, i, 167) and then treated with carbon disulphide and methyl iodide. The *methyl pinacolyl xanthate*,  $C_8H_{13}-O-CS-SMe$ , b. p.  $100^{\circ}/12$  mm.,  $D_4^{20} 1.0228$ , decomposes at  $160-175^{\circ}$ , and the purified *tert-butylethylene* [ $\gamma\gamma$ -dimethyl- $\Delta^2$ -butylene],  $CMe_3\cdot CH:CH_2$ , is a colourless liquid, having b. p.  $41.2-42^{\circ}/760$  mm.,  $D_4^{20} 0.6549$ , and  $n_D^{20} 1.37667$ . On oxidation with permanganate, acetone is not obtained, the chief product being  $\alpha$ -dimethylpropionic acid, whilst reduction with hydrogen in presence of platinum black results in the formation of  $\beta\beta$ -dimethylbutane.

J. C. W.

Decomposition of Heptyl Alcohol at 220° in the Presence of Finely Divided Nickel. JACOB BOESEKEN and G. H. VAN SENDEN (*Rec. trav. chim.*, 1913, 32, 23—38).—The authors have repeated the

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experiments described by van Beresteyn (A., 1911, i, 761), who obtained heptyl alcohol and a substance which he regarded as *n*-hexylene, by the reduction of heptaldehyde according to the general method of Sabatier and Senderens. Heptyl alcohol, under similar circumstances, was found to yield *n*-hexylene, carbon monoxide, and hydrogen, the course of the actions being represented by the equations:  $C_6H_{13}\cdot CHO + H_2 = C_6H_{13}\cdot OH$ ,  $C_6H_{13}\cdot OH = C_6H_{12} + CH_3\cdot OH$ ,  $CH_3\cdot OH = CO + 2H_2$ . On theoretical grounds, the authors consider this interpretation to be improbable, and are led to the conclusions: (1) that heptyl alcohol, in the presence of finely divided nickel at 220°, is decomposed into heptaldehyde and hydrogen; (2) that, particularly in the presence of an inert gas, the heptaldehyde is converted into *n*-hexylene, hydrogen, and carbon monoxide; (3) that *n*-hexylene combines with a considerable proportion of the liberated hydrogen to form *n*-hexane, and that, in the presence of an excess of hydrogen, all the *n*-hexylene undergoes reduction; (4) that heptaldehyde is not reduced in the presence of carbon dioxide, and only slightly reduced in an atmosphere of hydrogen; (5) that *n*-hexylene (mixed with *n*-hexane) is best obtained by the decomposition of heptaldehyde by nickel at 220° in a current of carbon dioxide, and (6) that *n*-hexane is obtained by the catalytic decomposition of heptyl alcohol or heptaldehyde by nickel at 220° in a current of hydrogen.

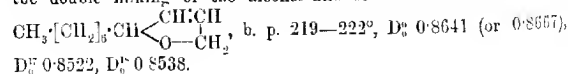
Heptyl alcohol was obtained by the reduction of heptaldehyde dissolved in glacial acetic acid by means of sodium amalgam. Small quantities of *3 di-n-heptylethylene glycol* [*n*-tetradecane- $\eta\theta$ -diol], b. p. 218°/14 mm., m. p. 69—70°, were obtained as by-product.

Heptyl alcohol, when passed over nickel at 220° in a current of hydrogen, yielded about 62% *n*-hexane, 17% of a mixture of heptyl alcohol and heptaldehyde, and carbon monoxide. In a current of carbon dioxide, however, it yielded about 14.5% *n*-hexylene, 31% *n*-hexane, 24% of a mixture of heptyl alcohol with a little heptaldehyde, carbon monoxide, and hydrogen, the change being represented by the equation:  $3C_6H_{13}\cdot OH = 2C_6H_{14} + C_6H_{12} + 3CO + 4H_2$ .

Heptaldehyde, at 220° in a current of carbon dioxide, gave about 24% *n*-hexylene, 29% *n*-hexane, 16% unchanged heptaldehyde, carbon monoxide, hydrogen, and possibly a trace of formaldehyde. The quantities of the products obtained agreed with the equation:  $100C_6H_{13}\cdot CHO = 45C_6H_{12} + 55C_6H_{14} + 100CO + 45H_2$ . At 180°, the course of the reaction was similar.

*n*-Hexane was not affected when passed over nickel at 220° in a current of carbon dioxide. H. W.

$\alpha\delta$ -Oxide from Undecyl Alcohol. N. A. Logginov (J. Russ. Phys. Chem. Soc., 1913, 45, 136—145).—The action of zinc chloride or 50% sulphuric acid on undecyl alcohol results in displacement of the double linking of the alcohol and formation of the  $\alpha\delta$ -oxide,



When zinc chloride is used, the oxide is accompanied by an unsaturated alcohol,  $C_{11}H_{22}O$ , b. p. 243–246°, which forms a crystalline phenylurethane,  $C_{15}H_{27}O_2N$ , m. p. 49.5°, and is being further investigated.  
T. H. P.

**Action of  $\alpha\beta$ -Dichloroethyl Ether on Mixed Magnesium Derivatives.** ROBERT LESPIEAU and BRESCH (*Compt. rend.*, 1913, 156, 710–712).— $\alpha\beta$ -Dichloroethyl ether condenses readily with magnesium derivatives of ethyl and allyl bromides and acetylene, giving products somewhat difficult to purify. The compound,



obtained from the acetylene derivative is a colourless liquid, b. p. 136–137°/12 mm., and is probably a mixture of two *cis*- and *trans*-isomerides (compare Dupont, A., 1910, i, 85). On bromination in chloroform, it yields two dibromides,  $C_{10}H_{16}O_2Cl_2Br_2$ , separable by their varying solubility, the less soluble one having m. p. 107–108°, and the other m. p. 71–72°. These are also probably *cis*- and *trans*-isomerides.  
W. G.

**Compounds of Ethyl Phosphite with Silver Haloids.** ALEXANDER F. AREBUZOV and A. V. KARTASCHOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 79–81).—Derivatives of trivalent phosphorus of the form  $PR_3$  or  $P(OR)_3$  form compounds with cuprous and platinumous haloids, and the authors find that ethyl phosphite forms similar compounds with silver haloids. These compounds form colourless, ribbon-like crystals, their melting points being:  $P(OEt)_3 \cdot AgCl$ , 4.5–5.5°;  $P(OEt)_3 \cdot AgBr$ , 40–40.5°;  $P(OEt)_3 \cdot AgI$ , 81–83°.  
T. H. P.

**Uranium Formate.** WILLIAM GEMISNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1913, [iv], 13, 221–223).—Uranium formate is a deliquescent, yellow salt, readily soluble in water. Attempts to estimate the water of crystallisation were unsuccessful, owing to the ready loss of formic acid from the salt on prolonged desiccation. When calcined in a closed vessel, the salt leaves a residue of pure uranous oxide, but, if an open vessel is used, traces of a higher oxide are formed. Similar results were previously obtained with uranium oxalate (A., 1912, i, 535).

When boiled with a large quantity of water, uranium formate is hydrolysed, hydrated uranium trioxide,  $UO_3 \cdot 2H_2O$ , separating as a yellow precipitate, which is converted by calcination into the green oxide,  $U_2O_5$ .

Uranium formate was exposed to diffused daylight during three months in the presence of methyl alcohol. A brown deposit of uranium oxide was thereby obtained, and the strongly acid methyl alcoholic solution was found to contain methyl formate.

Very little decomposition occurred in similar circumstances in the presence of ethyl alcohol. Very little formic acid was liberated, whilst the residue contained only small amounts of mono- and dihydrated uranium trioxide mixed with unchanged uranium formate.

H. W.

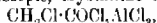
**Preparation of Halogen Formic Esters.** EMANUEL MEIER (D.R.-P. 254471).—The following halogen formic esters in addition to those previously described (this vol., i, 5) have now been prepared. *Dimethylethylcarbinyl chloro-formate*, a liquid which decomposes at 20° and cannot be distilled in a vacuum; the homologous *methyl-diethylcarbinyl chloro-formate* has similar properties. F. M. G. M.

**Distillation and Sublimation of Ammonium Salts under Diminished Pressure.** RICHARD ESCALES and HANS KOEPKE (*J. pr. Chem.*, 1913, [ii], 87, 258–279).—Of the normal salts examined the formate (*s*, 90–140°), acetate (*s*, 90°), thiocyanate (*d*, 165°), cyanate (*s*, 160–190°), nitrite (*s*, 70°), and sulphite (*s*, 70–120°) distil or sublime under a pressure of 10 mm. without decomposition, whilst the propionate (*d*, 70–75°), butyrate (*d*, 70–80°), glycolate (*d*, 160°), lactate (*d*, 140–150°), benzoate (*s*, 60–130°), and salicylate (*s*, 90–150°) are converted into the corresponding acid salts,  $\text{NH}_4\text{HX}$ ; the temperatures at which distillation or sublimation occurs are given in brackets (*s* denotes sublimation; *d*, distillation). When heated to 300°/10 mm., ammonium sulphate and persulphate lose ammonia, yielding the acid salts; ammonium thiosulphate sublimes at 70°/10 mm., the sublimate consisting of ammonium sulphite. Ammonium carbonate undergoes complete dissociation, whilst carbamide and thiocarbamide sublime in the form of ammonium cyanate and thiocyanate respectively. Of the acid salts,  $\text{NH}_4\text{HX}$ , the acetate (*d*, 67°), propionate (*d*, 73°), butyrate (*d*, 78°), glycolate (*d*, 160°), lactate (*d*, 145°), benzoate (*s*, 60–130°), salicylate (*s*, 90–150°), and hydrogen carbonate distil or sublime unchanged at 10 mm.

A mixture of normal or acid ammonium acetate and propionic acid in molecular proportions distils at 66–68°/10 mm., yielding the acid ammonium salt,  $\text{CH}_3\cdot\text{CO}_2\cdot\text{NH}_4\cdot\text{C}_2\text{H}_5\cdot\text{CO}_2\text{H}$ , which forms very deliquescent crystals, m. p. 42–43°, and is converted by distillation with butyric acid into the ammonium salt,  $\text{CH}_3\cdot\text{CO}_2\cdot\text{NH}_4\cdot\text{C}_2\text{H}_5\cdot\text{CO}_2\text{H}$ . This has m. p. 41°, b. p. 72–74°/10 mm., and is also obtained by distilling normal or acid ammonium acetate with butyric acid. F. B.

**Decomposition of Certain Acid Chlorides by Aluminium Chloride.** JACOB BOESKEX (*Rec. trav. chim.*, 1913, 32, 1–14).—In continuation of the work of Böeseken and Prius (*A.*, 1910, i, 152; 1911, i, 173), the action of aluminium chloride on the chlorides or sulphonyl chlorides of a number of halogenated acids has been investigated. Normal results were obtained with acid chlorides which did not contain hydrogen or a benzene group, but, in the presence of the latter, the reaction appeared to be complex, giving resinous products from which no definite compound could be isolated.

[With P. HASSELBACH.]—Monochloroacetyl chloride and aluminium chloride yielded a hygroscopic, crystalline compound,

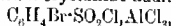


which, when heated alone or with carbon tetrachloride, evolved hydrogen chloride, leaving a charred residue. Carbon monoxide could not be detected in the gas evolved. When heated in chloroform solution at 80°, a small quantity of a substance, m. p. about 175°, was obtained, to

which no definite composition could be assigned. Similarly, aluminium chloride and chlorofumaryl chloride or  $\alpha:\beta:\beta:\beta$ -tetrachloropropionyl chloride yielded only charred or resinous products, from which a definite compound could not be separated.

[With (Mlle.) S. VAN DER TAS.]—*p*-Chlorobenzenesulphonyl chloride and aluminium chloride gave resinous products. The gases evolved contained hydrogen chloride and, generally, sulphur dioxide.

[With W. J. P. PELLE.]—*p*-Bromobenzenesulphonyl chloride and aluminium chloride yielded a crystalline additive product,



which, when heated at  $150\text{--}200^\circ$ , evolved sulphur dioxide and hydrogen chloride, and left a brown resin.

[With P. HASSELBACH.]—*Trichloroacrylyl chloride*, b. p.  $158^\circ/760\text{ mm.}$ , was obtained by the action of thionyl chloride on trichloroacrylic acid. When mixed with aluminium chloride in carbon disulphide solution, it yielded the compound,  $\text{CCl}_3\cdot\text{CCl}\cdot\text{COCl}\cdot\text{AlCl}_3$ , which, when heated in a current of dry air, gave only trichloroacrylyl chloride mixed with a little aluminium chloride, but no carbon monoxide. In the presence of aluminium chloride, trichloroacrylyl chloride reacted with benzene and its homologues to form quantitative yields of ketones of the type  $\text{R}\cdot\text{CO}\cdot\text{CCl}\cdot\text{CCl}_2$ , only the chlorine atom attached to the carbonyl group being replaced.

*Pentachloropropionyl chloride*, m. p.  $42^\circ$ , obtained from the preceding chloride by the action of chlorine in sunlight, when heated with aluminium chloride at  $60^\circ$  evolved carbon monoxide and carbonyl chloride, leaving a residue from which hexachloroethane and tetrachloroethylene were isolated, decomposition occurring according to the equations: (I)  $\text{CCl}_3\cdot\text{CCl}_2\cdot\text{COCl} = \text{CO} + \text{C}_2\text{Cl}_4$ , (II)  $\text{CCl}_3\cdot\text{CCl}_2\cdot\text{COCl} = \text{COCl}_2 + \text{C}_2\text{Cl}_4$ . When treated with aluminium chloride in the presence of benzene, *pentachloropropiophenone*,  $\text{COPh}\cdot\text{CCl}_2\cdot\text{CCl}_3$ , m. p.  $83^\circ$ , was obtained when the reaction was continued until one molecule of hydrogen chloride had been evolved. When, however, reaction was continued until two molecules of hydrogen chloride had been evolved, tetrachloroethylene and benzophenone were formed. The presence of the latter may be due to dissociation of pentachloropropionyl chloride into tetrachloroethylene and carbonyl chloride, and condensation of the latter with benzene, or pentachloropropiophenone may be decomposed by aluminium chloride into tetrachloroethylene and benzoyl chloride. The odour of the latter is perceptible when pentachloropropiophenone is warmed with a little aluminium chloride. H. W.

**Montanic Acid and its Derivatives.** HUGH RYAN and JOSEPH ADGAR (*Proc. Roy. Irish Acad.*, 1913, 30, 97–105. Compare A., 1909, i, 629).—The authors have prepared a series of derivatives of montanic acid, the formulae of which are in agreement with the formula,  $\text{C}_{28}\text{H}_{56}\text{O}_2$ , for montanic acid itself, thus confirming the previous work of Ryan and Dillon (A., 1909, i, 629), and Easterfield and Taylor (T., 1911, 99, 2302), in contrast to that of Hell (*Zeitsch angew. Chem.*, 1900, 13, 556), von Boyen (A., 1902, i, 72), and Eisenreich.

*Methyl montanate*, prepared by boiling montanic acid with methyl

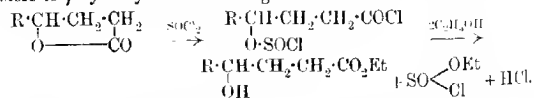
alcohol in the presence of sulphuric acid, crystallises in white, curved needles, m. p. 66°. The similarly crystallised *ethyl* and *n-propyl* esters have m. p. 64—65° and 63·5° respectively.

*Dimethylheptacosylcarbinol*,  $C_{27}H_{55} \cdot CMe_2 \cdot OH$ , obtained from methyl montanate and magnesium methyl iodide, has m. p. 63—64°, whilst the corresponding *diethyl* and *diphenyl* derivatives melt respectively at 59—60° and 58°. When ethyl montanate is treated with *p*-bromotoluene and the resulting product subjected to steam distillation, the residue is found to consist of the unsaturated hydrocarbon,  $C_{27}H_{34} \cdot C(C_6H_5Me)_2$ , m. p. 47°. When, however, the steam distillation is omitted and the product purified by repeated crystallisation from alcohol, it can be separated into two portions, the major part consisting of the above hydrocarbon, the minor part of *di-p-tolylheptacosylcarbinol*, m. p. 51—52°. The action of an ethereal solution of magnesium  $\alpha$ -naphthyl bromide on ethyl montanate appears to yield a mixture of *di- $\alpha$ -naphthylheptacosylcarbinol*, m. p. 57—58°, and, probably,  *$\alpha$ -naphthylheptacosyl ketone*,  $C_{27}H_{55} \cdot CO \cdot C_{10}H_7$ , m. p. 51—53°. These substances can be readily separated, since the former dissolves very sparingly in hot methyl alcohol, in which the latter is readily soluble.

Unsuccessful attempts were made to isolate *montanyl chloride* in the pure state by the action of phosphorus tri- or penta-chloride on montanic acid. The product obtained had m. p. 63—65°. It was transformed by concentrated aqueous ammonia into *montanamide*, m. p. 109°, small quantities of a substance, probably *montaonitrile*, m. p. 60—65°, being simultaneously formed.

Attempts to prepare *ceryl alcohol* from montanic acid were unsuccessful, owing to the difficulty of isolating *heptacosylmethylurethane* from the product of the successive action of bromine and sodium methoxide on montanamide. The converse operation (the preparation of montanic acid from *ceryl alcohol* by the malonic ester synthesis) could not be effected, since *cerylmalonic ester* could not be obtained from *ceryl iodide* and *sodiomalonic ester* under the most varied conditions. *Ceryl iodide*,  $C_{26}H_{52} \cdot I$ , m. p. 55—56°, was obtained by the action of iodine and red phosphorus on *ceryl alcohol*. H. W.

**Action of Thionyl Chloride on Certain Lactones.** PHILIPPE BARBIER and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 223—229).—A critical survey of the action of thionyl chloride on organic substances is given. The authors have investigated the effect of boiling certain  $\gamma$ -lactones (1 mol.) in benzene solution with thionyl chloride (1·1 mol.). The product of the reaction was poured into excess of methyl or ethyl alcohol and subsequently examined in the form of its methyl or ethyl ester. In these circumstances, thionyl chloride transforms the  $\gamma$ -lactones employed (except coumalin) into esters of  $\gamma$ -hydroxy-acids according to the scheme:



$\gamma$ -Valerolactone was transformed into ethyl  $\gamma$ -hydroxyvalerate.

b. p. 80—81°/12 mm. (compare Neugebauer, A., 1885, 651), from which a phenylurethane could not be obtained.

$\gamma$ -Phenyl- $\gamma$ -butyrolactone, m. p. 37—38°, b. p. 175—176°/11 mm. (Jayne, A., 1883, 472; Fittig and Leoni, A., 1898, i, 196), was prepared by the condensation of bromoacetophenone with ethyl sodiomalonate and saponification of the crude product with alcoholic sodium hydroxide at 160°. At the high temperature employed, the latter substance probably acted as a reducing agent. In addition, small quantities of benzylpropionic acid and of a neutral substance, m. p. 190—192°, probably a dilactone (annexed formula), were obtained. When acted on successively by thionyl chloride and ethyl alcohol,  $\gamma$ -phenyl- $\gamma$ -butyrolactone yielded *ethyl  $\gamma$ -hydroxy- $\gamma$ -phenylbutyrate*, b. p. 158—160°/17 mm.

Coumarin did not react with thionyl chloride under the conditions employed.

H. W.

#### Action of Thionyl Chloride on Certain Lactonic Acids.

PHILIPPE BARBIER and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 229—236. Compare preceding abstract).—The experimental conditions chosen were the same as those previously described (*loc. cit.*). In these circumstances, thionyl chloride does not cause a rupture of the lactonic grouping, the product of the reaction being the lactonic acid chloride. This result is not influenced by the use of an excess of thionyl chloride.

Methylparaconyl chloride, b. p. about 142°/10 mm., obtained by the action of thionyl chloride on methylparaconic acid, was converted by methyl alcohol into *methyl methylparaconate*, b. p. 145—146°/11 mm.

In similar circumstances, terebic acid slowly yielded the corresponding chloride, b. p. 143°/12 mm., from which *methyl terebate*, b. p. 148—149°/17 mm., was obtained.

$\beta\beta$ -Dimethylbutyrolactone  $\gamma$ -carboxylic acid (Petkin and Thorpe, T., 1899, 75, 56) gave the corresponding chloride, which, when treated with methyl alcohol, yielded the *methyl ester*, b. p. 149—150°/12 mm.

Similarly, terpenylic acid formed terpenyl chloride, methyl terpenylate, b. p. 145—147°/15 mm., and ethyl terpenylate, m. p. 37°/3, b. p. 174—177°/15 mm. Fittig and Levy (A., 1890, 873) give b. p. 305°/ordinary pressure, whereas Simon-en (T., 1907, 91, 187) found 169—171°/15 mm.

Phenylparaconyl chloride, prepared by the action of thionyl chloride on anhydrous phenylparaconic acid, m. p. 106°, 115°, or 121° (compare Jayne, A., 1883, 473; Fittig and Röders, A., 1890, 621) yielded, when decomposed by water, the acid, m. p. 99°. With methyl alcohol it yielded *methyl phenylparaconate*, m. p. 69—70°, b. p. 211°/14 mm. In the case of phenylparaconic acid, small quantities of polyphenylcrotonic acid, m. p. 179°, were also isolated.

The authors have attempted unsuccessfully to repeat the previously recorded transformation of terebic and phenylparaconic acids into the



anhydrides of *cis*-3:3-dimethylcyclopropane-1:2-dicarboxylic acid and *cis*-3-phenylcyclopropane-1:2-dicarboxylic acid (A., 1911, i, 722) under the action of thionyl chloride. They now attribute this result to the presence of some impurity in the specimen of thionyl chloride used, and point out that the substance is frequently contaminated with phosphoryl chloride, stannic chloride, sulphur trioxide, etc., to the presence of which the irregular results frequently obtained by the application of the reagent are ascribed. H. W.

$\gamma\gamma\gamma$ -Trichloro- $\beta$ -hydroxybutyric Acid and  $\gamma\gamma\gamma$ -Trichloro crotonic Acid. KARL VON AUWERS and M. SCHMIDT (*Ber.*, 1913, 46, 487—494. See following abstract).— $\gamma\gamma\gamma$ -Trichloro- $\beta$ -hydroxybutyric acid, m. p. 118—119° (von Thurnlackh, A., 1892, 429), is best obtained by gently boiling a mixture of malonic acid, chloral, and acetic acid for several hours; a certain specimen of malonic acid, although apparently normal in all other respects, always failed to give this reaction. The substance can be distilled almost undecomposed in small quantities, b. p. 181—188°/17 mm.; methyl ester, rhombohedral crystals, m. p. 61—62°, b. p. 135—136°/13 mm.; ethyl ester, silky needles, m. p. 56—57°, b. p. 143—144°/12 mm.; the acetyl derivative, needles, m. p. 97—99°, gives an oily methyl ester, b. p. 130°/13 mm.,  $D_4^{15}$  1.3937,  $n_D^{15}$  1.46815, and an oily ethyl ester, b. p. 134°/10 mm.,  $D_4^{15}$  1.3393,  $n_D^{15}$  1.46458. All endeavours to produce a substance,  $\text{OH}\cdot\text{CH}\cdot\text{CCl}_2\text{CO}_2\text{H} \rightarrow \text{O}$ , by elimination of hydrogen chloride from the trichlorohydroxybutyric acid were fruitless.

The method described by Kütz (A., 1907, i, 707) for the preparation of  $\gamma\gamma\gamma$ -trichlorocrotonic acid is found to yield the above trichlorohydroxybutyric acid, and the m. p. given for the substance (*loc. cit.*) agrees with that of this acid. It is now found that the elements of water can be eliminated from trichlorohydroxybutyric acid by heating with acetic anhydride and sodium acetate; the resultant  $\gamma\gamma\gamma$ -trichlorocrotonic acid forms needles, m. p. 113—114°, b. p. 143—146°/18 mm.; it immediately reduces potassium permanganate in the cold, and is rapidly decomposed by hot water with formation of hydrochloric acid. The potassium and silver salts were prepared, the latter of which when heated in benzene on the water-bath eliminates silver chloride with the formation of a mixture of substances mainly complex, but possibly containing a little of the lactone,  $\text{CH}\cdot\text{CCl}_2\text{CO}_2\text{H} \rightarrow \text{O}$ . The acid forms an oily methyl ester, b. p. 85.4°/12 mm.,  $D_4^{15}$  1.3968,  $n_D^{15}$  1.48975, and an oily ethyl ester, b. p. 100.5°/13 mm.,  $D_4^{15}$  1.3375,  $n_D^{15}$  1.48693.

From the above results it follows that the group  $-\text{CCl}_2$  exerts no special spectrochemical influence. D. F. T.

The Constitution of the Chlorides of 1:2- and 1:3-Dicarboxylic Acids. KARL VON AUWERS and M. SCHMIDT (*Ber.*, 1913, 46, 457—487).—The consideration of the spectrochemical effect of chlorine in organic substances (von Auwers, A., 1912, ii, 1015) is extended to the question of the structure of such acid dichlorides

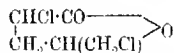
as succinyl and phthalyl chlorides (compare Scheiber, A., 1912, i, 559; Scheiber and Knothe, A., 1912, i, 701; Bredt, A., 1912, i, 411; Ott, A., 1912, i, 828). The decision of Brühl as to the symmetrical structure of phthalyl chloride (*Ber.*, 1907, 40, 884, 896) is based on too little experimental evidence to be entirely satisfactory; an investigation of the specific exaltations of the refractivity and dispersive power of various acid chlorides nevertheless indicates the correctness of this view.

A comparison of the chlorides and ethyl esters of crotonic, benzoic, and cinnamic acid shows that the exaltations in specific refractivity stand in the order acid > chloride > ester, whilst for the dispersion the exaltation is least for the ester, the free acid and the chloride being approximately equal. Phthalyl chloride shows no exceptional exaltation when compared with ethyl phthalate, the values in fact being in good agreement with those for the corresponding derivatives of benzoic acid; the results, however, when compared with those calculated for the unsymmetrical formula  $C_6H_4 \begin{smallmatrix} \diagup CCl_2 \\ \diagdown CO \end{smallmatrix} > O$  would indicate an improbably large exaltation.

The ethyl ester and chloride of fumaric acid exhibit exaltations approximately equal to those of the corresponding phthalic acid compounds; isophthalic ester and chloride have exaltations appreciably higher, but this is probably to be attributed to the effects of structure isomerism. Maleyl chloride could not be obtained sufficiently pure for spectrochemical investigation.

In order to throw further light on this question, most of the chlorides of the oxalic series of acids were examined from oxalic to sebacic acid, and no exaltation was observed except a trace in the case of oxalyl chloride which may be attributed to the  $-CO \cdot CO-$  group. Succinyl and glutaryl chloride must therefore be entirely of the symmetrical dichloride structure.

In the absence of pure, simple derivatives of the dichlorolactone molecule  $\begin{smallmatrix} CH \cdot CCl_2 \\ | \\ CH-CO \end{smallmatrix} > O$ ,  $\alpha$ ,  $\delta$  dichloro- $\gamma$ -valerolactone,



(Leuchs and Gina, A., 1912, i, 603, 604), was investigated and compared with the lactones of  $\delta$ -methoxy- and  $\delta$ -ethoxy- $\gamma$ -hydroxyvaleric acids, and with methyl  $\alpha\beta$ -butyleneoxide- $\delta$ -carboxylate. All were found to be optically normal. It is therefore probable that the hypothetical dichlorolactonic structure for succinyl and phthalyl chlorides would also be optically normal.

*d*-*cis*-Camphoryl, *l*-*trans*-camphoryl, *d*-chlorocamphoryl, and dehydrocamphoryl chlorides from their spectrochemical behaviour are probably all normal acid chlorides. The first and third named certainly exhibit a certain negative exaltation, but as this is also to be observed with the corresponding esters it probably arises from the *gem*-dimethyl groups (see this vol., ii, 261).

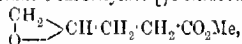
A comparison of the chlorides and esters of chlorofumaric and fumaric acids shows a similar exaltation in the chloride and ester

of each acid, thus indicating the normal symmetrical structure of the chlorides. With chloromaleyl chloride, however, the molecular refraction is below that of the isomeric chlorofumaryl chloride, and is in agreement with that calculated on theoretical grounds for the structure  $\begin{smallmatrix} \text{CH} \cdot \text{CCl}_2 \\ | \\ \text{CCl} - \text{CO} \end{smallmatrix} > \text{O}$ ; the lactonic formula is also favoured by a consideration of the molecular volume (Ott, *loc. cit.*). The structure of phthalyl chloride, on the other hand, is almost certainly the symmetrical one, as is indicated by recent chemical and physicochemical investigations (Scheiber, *loc. cit.*; Ott, *loc. cit.*) and by the present confirmation of Brühl's results. The constitution of the chlorides of the isomeric camphoric acids, chlorocamphoric acid, and dehydrocamphoric acid is also decided in favour of the symmetrical acid chloride form (compare Scheiber and Knothe, *loc. cit.*).

Succinyl chloride gave curiously variable results for density, refraction, and dispersion, probably due to some difficultly removable impurity; a specimen regarded as pure, indicated a true acid chloride structure, as already suggested by Ott.

The following substances were examined, but only the refraction for sodium light is quoted below; the original paper gives the values for the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -lines also.

Acetyl chloride, b. p. 51—52°,  $D_4^{20}$  1.1039,  $n_D^{20}$  1.38831; isovaleryl chloride, b. p. 114.5—115.5°, 771 mm.,  $D_4^{20}$  0.9854,  $n_D^{20}$  1.41361; crotonyl chloride, b. p. 117—120°/754 mm.,  $D_4^{20}$  1.0822,  $n_D^{20}$  1.46001; methyl  $\alpha/\beta$ -butyleneoxide- $\delta$ -carboxylate [ $\gamma$ - $\delta$ -oxidovalerate],



$D_4^{20}$  1.0731,  $n_D^{20}$  1.42589;  $\delta$ -methoxy- $\gamma$ -valerolactone,  $D_4^{20}$  1.1265,  $n_D^{20}$  1.44533;  $\delta$ -ethoxy- $\gamma$ -valerolactone,  $D_4^{20}$  1.0718,  $n_D^{20}$  1.44082;  $\alpha\delta$ -dichloro- $\gamma$ -valerolactone,  $D_4^{20}$  1.4367,  $n_D^{20}$  1.49624; oxalyl chloride, b. p. 60—61°,  $D_4^{20}$  1.4884,  $n_D^{20}$  1.43395; malonyl chloride, b. p. 58°/26 mm.,  $D_4^{20}$  1.4505,  $n_D^{20}$  1.45973; succinyl chloride, b. p. 88.8°/19 mm.,  $D_4^{20}$  1.3948,  $n_D^{20}$  1.47348; glutaryl chloride, b. p. 107—108°/16 mm.,  $D_4^{20}$  1.3221,  $n_D^{20}$  1.47281; suberyl chloride, b. p. 149—150°/12 mm.,  $D_4^{20}$  1.1718,  $n_D^{20}$  1.46847; sebacyl chloride, b. p. 168—170°/16 mm.,  $n_D^{20}$  1.46836; fumaryl chloride, b. p. 158—160°,  $D_4^{20}$  1.4117,  $n_D^{20}$  1.50038; chlorofumaryl chloride, b. p. 87—87.5°/28 mm.,  $D_4^{20}$  1.5653,  $n_D^{20}$  1.52172; ethyl chlorofumarate, b. p. 135—136°/17 mm.,  $D_4^{20}$  1.1886,  $n_D^{20}$  1.45782;

uns chloromaleyl chloride ( $\begin{smallmatrix} \text{CH} \cdot \text{CCl}_2 \\ | \\ \text{CCl} - \text{CO} \end{smallmatrix} > \text{O}$ , Ott, *loc. cit.*), b. p. 82.2—82.5°/26 mm.,  $D_4^{20}$  1.6055,  $n_D^{20}$  1.51362.

Benzoyl chloride,  $D_4^{20}$  1.2105,  $n_D^{20}$  1.55376; cinnamoyl chloride, b. p. 131°/20 mm.,  $D_4^{20}$  1.1617,  $n_D^{20}$  1.61364; phthalyl chloride, b. p. 156—157°/23 mm.,  $D_4^{20}$  1.4081,  $n_D^{20}$  1.57099; ethyl phthalate, b. p. 162—163°/7 mm.,  $D_4^{20}$  1.1202,  $n_D^{20}$  1.50293; isophthalyl chloride, m. p. 40—41°,  $D_4^{20}$  1.3880,  $n_D^{20}$  1.56999; ethyl isophthalate, b. p. 170—170.5°/24 mm.,  $D_4^{20}$  1.1239,  $n_D^{20}$  1.50815; *d*-cis-camphoryl chloride, b. p. 144.5—145.5°/17 mm.,  $D_4^{20}$  1.2446,  $n_D^{20}$  1.50133; ethyl *d*-cis-camphorate, b. p. 150—152°/8 mm.,  $D_4^{20}$  1.4318,  $n_D^{20}$  1.45613;

*l-trans*-camphoryl chloride, b. p. 153–154°/24 mm.,  $D_{25}^{25}$  1.2270,  $n_D^{25}$  1.49880; ethyl *l-trans*-camphorate, b. p. 155–157°/20 mm.,  $D_{25}^{25}$  1.0282,  $n_D^{25}$  1.45454; *d*-chlorocamphoryl chloride, b. p. 152–152.5°/17 mm.,  $D_{25}^{25}$  1.3219,  $n_D^{25}$  1.50797; *d*-dehydrocamphoryl chloride, b. p. 160–161°/32 mm.,  $D_{25}^{25}$  1.2176,  $n_D^{25}$  1.50433. D. F. T.

**Preparation of Terpenylic and Terebic Acids.** RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 166–169).—Tiemann and his collaborators (A., 1895, i, 548; 1896, i, 385; 1897, i, 84) have suggested that methoctylheptanonolide yields terpenylic acid on oxidation by chromic acid, and terebic acid when oxidised by nitric acid, and may be used as a source of these two acids. The author finds that on oxidation by nitric acid, terpenylic acid is the chief product (58.2% of the theoretical), the yield of terebic acid (18.6% of the theoretical) being small. The preparation and separation of the two acids are described. T. A. H.

**Attempts to Synthesise Monosubstituted Paraconic Acids.** PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 161–166. Compare A., 1911, i, 708).—The only method hitherto available for the preparation of these acids is that of Fittig (A., 1890, i, 583), which gives poor yields when aliphatic aldehydes are used. The authors have modified Reformatsky's reaction for the production of  $\beta$ -hydroxy-acids (A., 1896, i, 128) with a view to preparing monosubstituted paraconic acids by this means, but the yields are poor, only 7% of the theoretical yield of isopropylparaconic acid being obtained, and 12% of the calculated yield of hexylparaconic acid. The latter acid had m. p. 79–80°, which is 16° below that recorded by Schneegans. T. A. H.

**Preparation of Strontium Cholate.** KNOLL & Co. (D.R.P. 254530).—*Strontium cholate*,  $(C_{24}H_{39}O_5)_2Sr \cdot 10H_2O$ , colourless, hair-like tufts is readily obtained when an alcoholic solution of cholic acid is heated with an aqueous solution (or suspension) of strontium hydroxide; it has an important therapeutic action. F. M. G. M.

**Oxidation of Aldehydes by an Aqueous Solution of Bromine.** ERNEST ANDERSON (*Amer. Chem. J.*, 1913, 49, 179–184).—It is usually supposed that the method used for converting aldehydes into the corresponding acids by oxidation with aqueous solution of bromine is not applicable to the ordinary aldehydes. In order to test this question, several aldehydes have been subjected to the action of bromine, and the oxidation products isolated. The results show that whilst benzaldehyde, acetaldehyde, paraldehyde, and formic acid give good yields of the corresponding acids, namely, benzoic, acetic, and carbonic, formaldehyde and aldol are oxidised to only a small extent, and ethylaldehyde and chloral not at all.

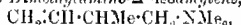
Acetaldehyde was found to give 71% of the theoretical yield of acetic acid; benzaldehyde, 80% of benzoic acid; paraacetaldehyde, 86% of acetic acid; and formic acid, 80% of carbonic acid. E. G.

**Glyoxal.** CARL D. HARRIS (*Ber.*, 1913, 46, 294—296. Compare A., 1907, i, 183).—Polymerisation of glyoxal is accelerated by the presence of moisture. When technical glyoxal which has been dried over phosphoric oxide at 95° is distilled alone, the unimolecular compound is obtained. It is claimed that Meisenheimer's depolymerisation of methylglyoxal (A., 1912, i, 831) was foreshadowed in the above-mentioned paper. J. C. W.

**Catalytic Preparation of Ketones.** JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1913, [viii], 28, 243—344).—A résumé of work already published (A., 1909, i, 286, 627; 1910, i, 11, 179, 489; 1911, i, 134, 302; 1912, i, 537). H. W.

**The Synthesis of Sugars by means of Radioactive Emanations.** JULIUS STOKLASA, JOHANN ŠENOR, and WENZEL ZDOBENICKÝ (*Compt. rend.*, 1913, 156, 646—648. Compare A., 1911, i, 178, 769).—As with ultra-violet rays, so under the influence of radium emanation hydrogen and carbon dioxide react in the presence of potassium hydrogen carbonate, giving formaldehyde, which in the presence of potassium hydroxide polymerises and gives reducing sugars. No formates could be detected during the reaction. The sugars formed are a mixture of hexoses giving phenylsazones, separable into two fractions, one, m. p. 198—199°, and the other, m. p. 178°. Unlike the sugars obtained in the photochemical synthesis under the influence of ultra-violet rays (compare A., 1912, i, 606), these sugars are optically active and have  $[\alpha]_D^{20} + 17.58^\circ$ . By distillation with hydrochloric acid indications of the presence of a pentose were obtained. W. G.

**Preparation of  $\delta$ -Dimethylamino- $\Delta^4$ -isomethylene and  $\delta$ -Dimethylamino- $\Delta^4$ -butylene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254529. Compare A., 1912, i, 742, 781; and Euler, A., 1897, i, 585).— $\delta$ -Dimethylamino- $\Delta^4$ -isomethylene,



a colourless liquid, b. p. 113—116°, and identical with the so-called " $\beta$ -methyl-dimethylpyrrolidino" (Euler, *loc. cit.*), can be prepared by heating  $\gamma$ -hydroxy- $\beta$ -methylbutyldimethylamino with concentrated sulphuric acid (3 parts) during three to four hours at 160°, or with 50% sulphuric acid (5—10 parts) during ten hours at 150—160°.

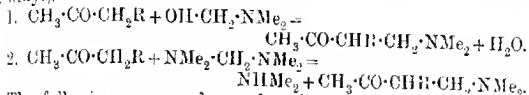
$\delta$ -Dimethylamino- $\Delta^4$ -butylene,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , a colourless liquid, b. p. 94—96°, is obtained in a similar manner from  $\gamma$ -hydroxy-butyldimethylamine with 20—30% sulphuric acid (5 parts) at 200° during ten hours.

These compounds have an odour of coniine, and find employment in the preparation of isoprene and erythene. F. M. G. M.

**Preparation of  $\delta$ -Dimethylamino- $\gamma$ -dimethylbutan- $\beta$ -ol.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254713).—When methyl tetramethyldiaminoisopropyl ketone (following abstract) is boiled during one hour with 20% sulphuric acid (4—6 parts), it furnishes dimethylamino- $\beta$ -acetyllallene,  $\text{CH}_2\text{:C}(\text{Ac})\text{CH}_2\cdot\text{NMe}_2$ , which

on reduction gives rise to  $\delta$ -dimethylamino- $\gamma$ -methylbutan  $\beta$  ol (A., 1911, i, 598), a colourless oil, b. p. 67°–69°/17 mm. F. M. G. M.

**Preparation of Amino- and Diamino-ketones of the Aliphatic Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 254714. Compare A., 1911, i, 598, and preceding abstract).—When dimethylaminomethyl alcohol,  $\text{OH}\cdot\text{CH}_2\cdot\text{NMe}_2$ , or tetramethyldiaminomethane,  $\text{Me}_2\text{N}\cdot\text{CH}_2\cdot\text{NMe}_2$ , are condensed with acetone (or its homologues), the following reactions take place (R = hydrogen or alkyl).



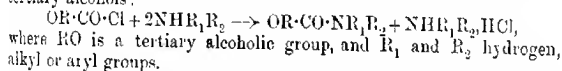
The following compounds are described: dimethyl- $\beta$ -acetylpropylamine (*loc. cit.*), b. p. 51°–51.5°/13 mm.

$\beta$ -Acetyltrimethyltetramethylenetetramethyldiamine [methyl tetramethyldiaminotert. butyl ketone],  $\text{CH}_3\cdot\text{CO}\cdot\text{CMe}(\text{CH}_2\cdot\text{NMe}_2)_3$ , a colourless, viscous oil, b. p. 110°–112°/18 mm., from methyl ethyl ketone and dimethylaminomethyl alcohol.

$\beta$ -Acetyldiethyltrimethylamine [methyl dimethylaminoethyl ketone],  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , a colourless oil with a strong ammoniacal odour, b. p. 57°–58°/18 mm.; and  $\beta$ -acetyltrimethyltetramethylenetetramethyldiamine [methyl tetramethyldiaminoisopropyl ketone],  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{NMe}_2)_2$ , a colourless, odourless, viscous oil, b. p. 96°–98°/16 mm.

These compounds are employed in the preparation of erythrene and isoprene. F. M. G. M.

**Preparation of Urethanes of Tertiary Alcohols.** EMANUEL MERCK (D.R.-P. 254472. Compare this vol., i, 5).—It is found that the halogen formyl esters described previously can be readily converted by the action of ammonia or substituted ammonias into urethanes of tertiary alcohols:



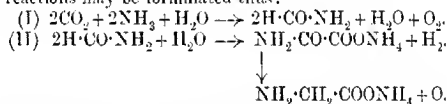
Dimethylethylcarbonyl chloro-formate with alcoholic ammonia furnishes a urethane, colourless needles, m. p. 85°–87°; an ethyl urethane, a colourless oil, b. p. 86°/13 mm., and 86°/11 mm.; a phenyl urethane, colourless crystals, m. p. 44°–47°, b. p. 146°/9 mm.; a methylphenylurethane, a colourless oil, b. p. 133°/13 mm., and with *p*-phenetidine a *p*-ethoxyphenylurethane, colourless needles, m. p. 88°–90°, whilst methyldiethylcarbinol gives rise to a urethane, colourless needles, m. p. 61°, and a phenylurethane. F. M. G. M.

**Behaviour of Formamide Under the Influence of the Silent Electric Discharge.** The Question of Nitrogen Assimilation. WALTHER LÖB (*Ber.*, 1913, 46, 684–697).—In the course of some experiments on the influence of the silent electric discharge on various combinations of moist carbon dioxide, carbon monoxide,

alcohol and ammonia, with or without oxygen or air, the only compound obtained which could be regarded as of interest to the problem of nitrogen assimilation was hexamethylenetetramine (A., 1909, i, 760). Further investigations on the behaviour of this compound towards oxidising and reducing agents, and towards living yeast, showed that it had no relation to the amino-acids, and, therefore, throws no light on the general question. The discovery of Losanitsch and Jovitschitsch (A., 1897, i, 179) that ammonia and carbon monoxide produce formamide led the author to regard this compound as an intermediate stage, and to try the effect of the silent discharge on the dry substance and on an aqueous solution, both boiling under reduced pressure. In the former case, oxamide was deposited on the sides of the discharge tube, and in the latter, as would be expected, ammonium oxamate. Some reduction was therefore necessary in order to arrive at glycine. Previous experience had shown that water itself is a reducing agent under these conditions (A., 1906, ii, 324), whilst the reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$  had also to be considered. The resolution of some formamide into carbon monoxide and ammonia was to be expected, and, indeed, an examination of the gases liberated during the experiment proved the presence of these substances. The existence of glycine in the product, after the removal of ammonia, was unquestionably demonstrated by the formaldehyde test of Sørensen, the "deaminising" method of van Slyke, the reaction with triketohydrindene hydrate, and the formation of the naphthalenesulphonyl compound (E. Fischer and Bergell, A., 1903, i, 24).

The presence of glycine could also be observed on repeating the experiment with moist carbon monoxide and ammonia. The formation of glycine from carbon dioxide (which breaks down into carbon monoxide under the influence of the silent discharge), ammonia, and water is therefore a process of reduction, and the oxidation of glycine should lead to these or intermediate products. Halley has shown that the products of the action of permanganate do, indeed, include formamide and oxamic acid (A., 1898, ii, 529).

The reactions may be formulated thus:



Reference must be made to the original paper for the experimental details, but it may be said that the amount of oxamide accumulated during twenty hours from 20 grams of dry formamide, boiling at  $110^\circ/15$  mm., was about 0.05–0.08 gram, whilst about 0.01 gram of ammonium oxamate was obtained from a 5–10% solution during the same time, the glycine present being comparable with a 0.01% solution.

J. C. W.

**The Diamide of Sulphoisobutyric Acid.** JACOB MOLL VAN CHARANTE (*Rec. trav. chim.*, 1913, 32, 90–96. Compare A., 1905, i, 16).—Sulphoisobutyroldiamide,  $\text{NH}_2\cdot\text{SO}_2\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}_2$ , was obtained by passing ammonia into a cold methyl-alcoholic solution of methyl

chlorosulphoisobutyrate. It decomposed without melting at about  $340^{\circ}$ . At  $17^{\circ}$ , one part of diamide dissolved in 201.8 parts of water, whilst at  $100^{\circ}$  the solubility was one part in 24.9. It was insoluble in the other usual solvents. Attempts to condense it with carbonyl chloride, in the presence or absence of a catalyst, were unsuccessful. Similarly, oxalyl chloride, alone or in benzene solution, was without action on it.

To determine whether it was possible to cause a sulphonamide to react with oxalyl chloride, a solution of benzenesulphonamide and oxalyl chloride in benzene was boiled during two and a-half days. Hydrogen chloride was slowly evolved, and *diphenylsulphonamide*,  $C_6O_5(NH\cdot SO_2Ph)_2$ , formed. It had m. p.  $256^{\circ}$  (corr., slight decomp.).

H. W.

**Extraction of Glutamic Acid Hydrochloride and Betaine Hydrochloride from Molasses Residue.** HUGO STOLTZENBERG (*Ber.*, 1913, 46, 557—566. Compare A., 1912, i, 680).—Molasses residue is mixed with hydrochloric acid and subsequently saturated with hydrogen chloride. The crude hydrochlorides which are precipitated are treated with alcohol and hydrogen chloride, whereby glutamic acid hydrochloride is converted into the readily soluble ester hydrochloride. The solution of the latter is concentrated to a syrup, the residue boiled with water, the solution filtered from humin, decolorised, and concentrated until crystallisation begins, when it is again saturated with hydrogen chloride, whereby glutamic acid hydrochloride is precipitated. This has m. p.  $213^{\circ}$  when rapidly heated, and is shown to be partly racemised, the highest observed value for  $[\alpha]_D^{20}$  being  $+26.15^{\circ}$  in 10% hydrochloric acid solution, whereas Siegfried and Schutt (A., 1912, i, 952) observed  $+34.80^{\circ}$ . Purification by transformation into the barium salt and subsequent reprecipitation of the hydrochloride effected no improvement. The filtrates obtained after removal of glutamic acid hydrochloride deposited, on evaporation, betaine hydrochloride, and contained also a strongly acid substance, which could not be obtained in the crystalline state.

The remainder of the paper consists of a reply to the criticisms brought by Ehrlich (A., 1912, i, 835) against the previous work of the author (*loc. cit.*). Stoltzenberg's process of isolating betaine hydrochloride from molasses differs essentially from that of Ehrlich (1904, D.R.P. 157173), in that hydrochloric acid and alcohol are employed in the given order in the former process, in the inverse order in the latter. In the second method, the chemical nature of the residue is not affected by agitation with alcohol, and the hydrogen chloride is only used to precipitate the hygroscopic betaine. In the first method, however, the composition of the residue itself is greatly altered by the action of the hydrogen chloride. Ehrlich's statement that the alcohol consumption is less in his process than in that of the author is incorrect.

The paper concludes with a critical survey of the historical development of the subject as described by Ehrlich. H. W.

**Action of Sodium Hypobromite on Semicarbazide.** ROBERT STOLL (*Ber.*, 1913, 46, 260. Compare Finch, T., 1912, 101, 1755).

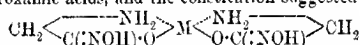
VOL. CIV. i.

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—The product of the action of sodium hypobromite on semicarbazide is hydrazodicarbonamide, and not *p*-urazine as described by Litch. The compound obtained on oxidation with chromic acid is therefore azodicarbonamide (Thiele, A., 1892, 1295 and 1430), and not a stable tetraziro. J. C. W.

**Salt- and Complex Salt-Formation with Amino- and Hydroxy-acetohydroxamic Acids.** HEINRICH LEY and F. MÄNNCHEN (*Ber.*, 1913, 46, 751–758).—On account of the similarity in structure between the carboxylic and hydroxamic acids, the authors have investigated certain derivatives of the latter in which the formation of complex salts was to be expected. It is found that internally complex salts are obtainable from amino- and hydroxy-hydroxamic acids somewhat analogous to those obtained from the simple amino-acids. To the normal copper salts is attributed the structure  $R \cdot C \begin{smallmatrix} \nearrow NO \\ \searrow O \end{smallmatrix} Cu$ ; acid salts could be obtained only from substituted hydroxamic acids, and the constitution suggested is



(compare Ley, A., 1909, i, 138), where M represents a bivalent metal atom. Complex salts containing a bivalent metal together with an alkali metal could be obtained both from the unsubstituted and substituted acids; the heavy metal is present as part of a complex ion, but from the colour of the salts of the amino- and hydroxy-substituted acids the conclusion is drawn that this atom is also linked with the anion complex by supplementary partial valencies.

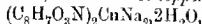
*Aminoacetohydroxamic acid*,  $NH_2 \cdot CH_2 \cdot C(OH) \cdot N \cdot OH$ , was obtained by the interaction of equimolecular quantities of hydroxylamine, ethyl aminoacetate, and sodium ethoxide in alcoholic solution; it was precipitated as the copper salt and recovered by the action of hydrogen sulphide; it is a colourless, crystalline solid, m. p.  $107^\circ$  (approx.); normal *copper* salt, green, amorphous powder, obtained by mixing aqueous solutions of the acid and copper acetate; *acid copper* salt, obtained by adding copper acetate to a solution of the *sodium* salt, separates in violet crystals; *acid nickel* salt, prepared by the addition of dilute sodium hydroxide solution to a solution of nickel acetate with a bimolecular quantity of the acid, forms deep red crystals; the complex *sodium nickel* salt,  $(C_2H_4O_2N_2)_2NiNaH_2O$ , yellowi-b-red, rhombic tablets, was obtained by treating a solution of the sodium salt with nickel acetate and sodium hydroxide.

*Anilinoacetohydroxamic acid*,  $NHPh \cdot CH_2 \cdot C(OH) \cdot N \cdot OH$ , colourless needles, m. p.  $126^\circ$  (decomp.), separates in the form of the *sodium* salt when ethyl anilinoacetate is treated in alcoholic solution with an equimolecular quantity of hydroxylamine; *copper* salt, green, amorphous solid.

*Phenylglycolohydroxamic acid*,  $OH \cdot CHPh \cdot C(OH) \cdot N \cdot OH$ , colourless, rhombic leaflets, m. p.  $132^\circ$ , was prepared in a similar manner to the last; *sodium* salt, needles; the green *copper* salt, like that of the last acid, gives a violet solution in aqueous sodium hydroxide; the *nickel* *sodium* salt could be obtained only as a reddish-yellow solution.

The free acid soon decomposes in solution with the formation of benzaldehyde.

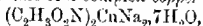
*Phenoxyacetaldehydoxamic acid*,  $\text{OPh}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ , prepared in an analogous manner from ethyl phenoxyacetate, forms colourless leaves, m. p.  $114^\circ$ ; the addition of copper acetate and sodium hydroxide solution to the solution of the sodium salt causes the formation of the crystalline, bluish-violet *copper sodium salt*,



which is converted by water into the green *copper salt*.

The interaction of equimolecular quantities of hydroxylamine, ethyl lactate, and sodium ethoxide in alcoholic solution produces unstable *sodium lactohydroxamate*,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{ONa})\cdot\text{NOH}$ .

An aqueous solution of acetohydroxamic acid (Miolati, A., 1892, 699) when treated with copper acetate and sodium hydroxide, after some days, deposits blue crystals of a complex *copper sodium salt*,



which is converted by water into the ordinary green copper salt.

D. F. T.

#### New Method of Preparing Nitriles of the Aliphatic Series.

ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 74—79).

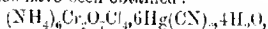
—Catalytic decomposition of the hydrazones of aliphatic aldehydes in presence of cuprous chloride, platinous chloride, or zinc chloride always yields nitriles to some extent, although the yield varies considerably. In general, hydrazones containing small radicles give very small proportions of nitriles, the decomposition then yielding principally substituted indoles and other compounds (see this vol. i, 388). On the other hand, hydrazones containing large radicles, such as *isovaleraldehydephenylhydrazone*, undergo nitrilic decomposition almost exclusively:  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{NHPh} \rightarrow \text{NH}_2\text{Ph} + \text{C}_5\text{H}_9\text{N}$ .

*isoValeronitrile*, thus obtained in 56% yield, is a colourless, mobile liquid, b. p.  $128.5^\circ$ , or  $52.5\text{—}53/50$  mm.,  $D_4^{20}$  0.7884,  $D_4^{25}$  0.8054 (compare Erlenmeyer, *Annalen*, 1871, 160, 266).

*isoButyronitrile* is similarly obtained from *isobutaldehydephenylhydrazone* in 37% yield, and *n*-heptonitrile, b. p.  $133.5^\circ$ ,  $D_4^{20}$  0.8107 (compare Henry, A., 1905, i, 561), from *n*-heptaldehydephenylhydrazone.

T. H. P.

**Chromates and Mercuric Cyanide.** DANIEL STROMHOLM (*Zeitsch. anorg. Chem.*, 1913, 80, 155—160. Compare A., 1912, ii, 618). The following compounds have been obtained:



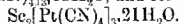
long, reddish-yellow crystals, with only a narrow range of stability;  $2\text{K}_2\text{CrO}_4\cdot 3\text{Hg}(\text{CN})_2\cdot 2\text{H}_2\text{O}$ . A chloride-chromate salt has not been obtained in the case of potassium.

C. H. D.

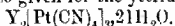
**Potassium  $\beta$ -Ferricyanide.** HORACE L. WELLS (*Amer. Chem. J.*, 1913, 49, 205—206).—Hauser and Biesalski (this vol. i, 26) have stated that the potassium  $\beta$ -ferricyanide described by Locke and Edwards (A., 1899, i, 407) is merely the ordinary salt, contaminated with colloidal Prussian-blue. It is now shown that this view is incorrect, and that Hauser and Biesalski have overlooked the fact that the

$\beta$  ferricyanide does not yield a precipitate with bismuth nitrate, and is thus readily distinguished from the ordinary salt. E. G.

**Crystalline Form of Two Scandium Platinocyanides.** PETER N. TSCHIRVINSKI (*Zeitsch. Kryst. Min.*, 1913, 52, 44—47).—The crystalline form, as observed under the microscope, is described for the yellow salt,  $\text{Sc}_2[\text{Pt}(\text{CN})_6]_3 \cdot 18\text{H}_2\text{O}$ , and for the red salt,



New observations are also given for the yttrium salt,



L. J. S.

**Magnesium Methyl Iodide.** PIERRE JOLIBOIS (*Compt. rend.*, 1913, 156, 712—714. Compare A., 1912, i, 675, 753).—The action of methyl iodide on magnesium in dry ether is a simple one, there being practically no secondary reaction under any conditions. The magnesium methyl iodide, so obtained, when heated in a vacuum, first loses its ether of constitution at  $130^\circ$ , and at  $240^\circ$  methane is evolved, according to the equation:  $2\text{MgMe}, \text{MgI}_2 = 3\text{CH}_4 + \text{Mg}_2\text{C}, 2\text{MgI}_2$ .

By raising the temperature to  $600^\circ$  no more gas is evolved. The residue is a voluminous, yellow mass, from which only a definite portion of the iodine can be extracted in the form of magnesium iodide by dry ether, leaving a compound, having the definite composition  $\text{Mg}_2\text{C}, \text{MgI}_2$ , which is violently decomposed by water with development of light and heat, and, on controlled decomposition by moist ether, yields practically pure methane. W. G.

**The Catalytic Hydrogenation of Camphorone.** Some New *cyclopentane* Hydrocarbons. MARCEL COUCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, 156, 470—473).—Camphorone on hydrogenation in the presence of reduced nickel at  $130^\circ$  yields dihydrocamphorone (compare Semmler, A., 1904, i, 260). If the reduction is carried out at  $280^\circ$ , the product obtained is 1-methyl-3-isopropylcyclopentane,  $\text{C}_9\text{H}_{18}\text{MePr}^2$ , a liquid with a terpene-like odour, b. p.  $132$ — $134^\circ$ ,  $D_{20}^{25}$  0.773,  $n_D^{20}$  1.4250. The same compound is obtained by dehydrating 1-methyl-3-isopropylcyclopentane-2-ol with zinc chloride, which furnishes a mixture of two isomeric unsaturated hydrocarbons, b. p.  $143$ — $145^\circ$ ,  $D_{20}^{25}$  0.786,  $n_D^{20}$  1.4465, non-separable, but which on hydrogenation at  $170^\circ$  are converted into the pentane hydrocarbon.

Dihydrocamphorone reacts with magnesium methyl iodide, giving a mixture of 1:2-dimethyl-3-isopropyl- $\Delta^1$ - and - $\Delta^2$ -cyclopentenes, b. p.  $150$ — $155^\circ$ ,  $D_{20}^{25}$  0.812,  $n_D^{20}$  1.4500, which on hydrogenation at  $180^\circ$  are transformed into 1:2-dimethyl-3-isopropylcyclopentane, b. p.  $146$ — $148^\circ$ ,  $D_{20}^{25}$  0.786,  $n_D^{20}$  1.4337. Similarly by using magnesium isopropyl iodide a mixture of 1-dimethyl-2:3-diisopropyl- $\Delta^1$ - and - $\Delta^2$ -cyclopentene, b. p.  $160$ — $168^\circ$ ,  $D_{20}^{25}$  0.812,  $n_D^{20}$  1.4509, is obtained, yielding on hydrogenation at  $180^\circ$ , 1-methyl-2:3-diisopropylcyclopentane, b. p.  $150$ — $152^\circ$ ,  $D_{20}^{25}$  0.781,  $n_D^{20}$  1.4318. W. G.

**The cycloOctane Series. VI. cycloOctatetraene.** RICHARD WILLSTÄTTER and MICHAEL HEIDELBERGER (*Ber.*, 1913, 46, 517—527. Compare Willstätter and Waser, A., 1912, i, 17).—The previous

observations with *cyclooctatetraene* have been repeated and extended. The quaternary ammonium base is now distilled in a still lower vacuum and at a correspondingly lower temperature (30–45°). On cooling, the hydrocarbon solidifies to a pale yellow, crystalline mass, m. p. –27°. It forms an additive compound with bromine, taking up two atoms only. The *dibromide*,  $C_8H_8Br_2$ , crystallises in lustrous, snow-white needles, m. p. 70–71·5° (corr.). It decolorises permanganate instantaneously and tends to take up more bromine, but hydrogen bromide is then eliminated, and a *substance*,  $C_8H_7Br$ , m. p. 53–55°, is obtained instead of the tetrabromide.

The tetraene reacts immediately with chlorine, and hydrogen chloride is eliminated; an oily *chloride* is obtained, and can be separated into two fractions, both of which have the composition  $C_8H_7Cl$ .

With hydrogen bromide in acetic acid solution the tetraene forms a *hydrobromide*,  $C_8H_9Br$ , which is an almost colourless oil with a sweet odour, b. p. 85–87°/12·5 mm. It slowly decomposes in presence of oxygen, and gives an orange coloration with concentrated sulphuric acid.

The molecular refraction of *cyclooctatetraene* shows little or no exaltation. Similarly, the molecular dispersion ( $\beta$ - $\alpha$ ) shows no marked exaltation, although in consequence of the greater dispersion in the ultra-violet the molecular dispersion,  $M_\gamma - M_\alpha$ , shows a larger exaltation.

The tetraene behaves, like benzene, optically normal in regions where it is free from absorption; the dispersion is, however, abnormal in the region where selective absorption takes place.

Such selective exaltation of the molecular dispersion is even more marked in the case of the yellow fulvenes; data are quoted for methylethylfulvene and dimethylfulvene, as well as *cyclooctatriene*.

When *cyclooctatetraene* is hydrogenated by the platinum method the yellow colour disappears after the addition of 1·5 molecules of hydrogen. The first three molecules appeared to be absorbed in approximately equal times and the fourth more slowly, the actual figures being 35, 40, 40, and 95 minutes respectively.

Methylethylfulvene does not lose the yellow colour until reduction is nearly complete. The three molecules of hydrogen were absorbed in 7, 7, and 10 minutes.

The product, *sec-butylcyclopentane*, is a mobile liquid, with an odour like limonene, b. p. 152–154°/725 mm.,  $D_{20}^{20}$  0·810.

The *cyclooctane* formed even from pure *cyclooctatetraene* is not pure, and probably contains an isomeride.

Pure *cyclooctatetraene* may be kept for several months without decomposition.

E. P. A.

[Preparation of *cycloHexene*.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 254473. Compare A., 1899, i, 22; 1902, i, 2, and T., 1898, 73, 941).—When the vapour of chlorocyclohexane at 350–450°/15–20 mm. is conducted over a catalytic agent (such as barium chloride, aluminium oxide, or nickel chloride), it gives rise to *cyclohexene*.

F. M. G. M.

**Rational Preparation of Some Benzene Homologues.** II. FRANZ KUNCKELL and GEORG ULEX (*J. pr. Chem.*, 1913, [ii], 87, 227—236).—A continuation of previous work (this vol., i, 29) on the preparation of benzene homologues by the interaction of alkyl esters of chloro-formic acid with aromatic hydrocarbons in the presence of aluminium chloride.

Methyl chloro-formate reacts with benzene to form toluene and *m*-xylene; with toluene it yields *p*-xylene and  $\phi$ -cumene.

The interaction of ethyl chloro-formate with benzene and toluene yields respectively *p*-diethylbenzene and 1-methyl-3:4-diethylbenzene, b. p. 200—203°, the constitution of which has been established by its oxidation to 4-methylphthalic acid.

*m*-Xylene reacts with ethyl chloro-formate, yielding 1:3-diethyl-5-ethylbenzene, b. p. 182—188°, and with *p*-xylene to form 1:4-diethyl-2-ethylbenzene, b. p. 183—185°.

The interaction of cumene with methyl and ethyl carbonates yields dimethylisopropylbenzene, b. p. 195—210°, and diethylisopropylbenzene, b. p. 250—256° respectively.

The addition of isobutyl chloro-formate to a mixture of aluminium chloride and benzene gives rise to *tert*-butylbenzene, whilst the addition of aluminium chloride to a mixture of the ester with benzene yields *di*-(*tert*.)butylbenzene, b. p. 225—235°, and *tri*-(*tert*.)butylbenzene.

The preparation of a *p*(1)-methylbutylbenzene, b. p. 190—195°, and a methyl*di*butylbenzene, b. p. 241—247°, from toluene and isobutyl chloro-formate, and *p*-methylamylbenzene, b. p. 205—210°, from amyl chloro-formate and toluene is also described.

F. B.

**Chemical Action of Light.** XXV. Autoxidations. III. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1913, 46, 417—422).—A continuation of the investigation of the autoxidation of aromatic hydrocarbons (*A.*, 1912, i, 174, 615). The results are in accordance with those of Suida (*A.*, 1912, i, 957), but as the present authors gave prolonged exposure to light and investigated only the final products, indications of peroxides were but rarely observed.

Benzene in contact with water and oxygen is completely unaltered after several months' exposure to sunlight (compare Suida, *loc. cit.*).

Ethylbenzene under similar conditions gives a yellow aqueous layer, and after neutralisation with sodium carbonate, ether extracts acetophenone with some unchanged ethylbenzene; the former was characterised by its semicarbazone; this, it was observed, separates from methyl alcohol with one molecule of alcohol of crystallisation, which is lost on drying over sulphuric acid. The alkaline solution, which had been extracted with ether, was found to contain formic and benzoic acids.

Mesitylene, when treated similarly, gave a strongly acidic mixture, which after neutralisation yielded an ethereal extract containing mainly unchanged hydrocarbon, together with a small quantity of a non-volatile substance and a trace of an aldehyde. The aqueous liquid on acidification gave formic acid, mesitylenic acid, a substance probably

\* and *Atti. R. Acad. Lincei*, 1913, [v], 22, i, 127—132.

a polycarboxylic acid which sublimed near  $300^{\circ}$ , and some resinous matter.

The oxidation product of  $\psi$ -cymene contained as its neutral constituents only unchanged hydrocarbon and a trace of an aldehydic substance; the acidic constituents comprised formic acid, together with 3:4-dimethylbenzoic acid, 2:4-dimethylbenzoic acid, and a difficultly volatile, crystalline substance; the presence of 2:5-dimethylbenzoic acid could not be detected.

Indene was practically completely changed, and the reaction mixture slowly gave the reaction for a peroxide. A relatively large amount of resinous matter was produced which was partly soluble in ether, the soluble portion being separable by boiling water into a colourless substance, crystallising in leaflets, m. p.  $72^{\circ}$ , and a yellow, amorphous substance, m. p.  $123^{\circ}$  (approx.). The acidic portion of the reaction product contained formic and phthalic acids, together with a third substance, m. p.  $174^{\circ}$ , probably homophthalic acid.

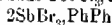
Naphthalene proved quite resistant to autoxidation, but tetrahydronaphthalene (Bamberger and Kitschelt, A., 1899, 1146) is readily oxidised, giving much resinous matter and a little phthalic acid.

D. F. T.

**Influence of Substituents in Benzene on the Binary Systems. Substituted Benzene-Antimony Trihaloids.** BORIS S. MESSCHUTKIN (*J. Chim. phys.*, 1912, 10, 598-611. Compare A., 1912, i, 98, 99, 100, 177).—The compounds of benzene with antimony trichloride and tribromide are of the type  $2SbCl_3.C_6H_6$ , but some substituted benzenes give in addition compounds of the type  $SbCl_3.PhR$ . Methyl-, ethyl-, propyl- and isomyl-benzenes exhibit a decreasing stability in the compounds  $2SbCl_3.PhR$ , whereas the stability of the compounds  $SbCl_3.PhR$  attains a maximum in ethylbenzene.

Antimony tribromide has less affinity for the phenyl nucleus than the chloride. Toluene gives compounds of both types, but ethyl-, propyl- and isomyl-benzenes of the type  $SbBr_3.PhR$  only, the ethyl compound again having the maximum stability.

Diphenyl forms the compounds  $2SbCl_3.PhPh$  (stable) and



(unstable), and diphenylmethane gives two stable compounds of the same types. Triphenylmethane, however, does not combine with antimony tribromide, and with the chloride gives only an unstable compound of the formula  $SbCl_3.CHPh_3$ .

The xylenes form with antimony trichloride compounds of both types, which are intermediate in stability between those of toluene and ethylbenzene. *p*-Xylene gives the most, and *m*-xylene the least, stable. With antimony tribromide, *p*-xylene gives only the compound  $2SbBr_3.C_6H_4Me_2$ , which is intermediate in stability between those of benzene and toluene, whilst *m*- and *o*-xylene give also compounds,  $SbBr_3.C_6H_4Me_2$ , which are less stable than that of toluene.

The compounds of antimony trichloride and tribromide with cymene are analogous in composition and inferior in stability to those of *p*-xylene. The unfavourable influence of the isopropyl group is thus manifest in presence of the methyl group.

Mesitylene and  $\psi$ -cumene form compounds of both types with antimony trihaloids, those of  $\psi$ -cumene being less and those of mesitylene more stable than the toluene compounds. Apparently the three methyl groups in mesitylene neutralise each other's effects on the phenyl nucleus.

R. J. C.

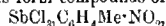
**Influence of Substituents in Benzene on the Properties of the Binary Systems Formed by Substituted Benzenes and Antimony Trichloride or Tribromide.** BORIS N. MENSCHUTKIN (*J. Chim. phys.*, 1912, 10, 612—623. Compare A., 1912, i, 193).—The compounds of monosubstituted benzenes with antimony trichloride are all of the two types  $2SbCl_3 \cdot PhR$  and  $SbCl_3 \cdot PhR$ . When R is H, OH, Me, OMe, Et,  $Pr^*$  or  $C_2H_5$ , both compounds are formed. When R is ORt, Bz, Ph, COH, COMe, CPh, CN, compounds of the second type only are produced. When R is  $NO_2$ , F, Cl, Br, I,  $CHPh$ , compounds of the second type are also produced, which, however, decompose on melting, and when R is  $SO_2H$ ,  $CO_2H$ , or COCl no combination occurs.

From the behaviour of phenol and anisole it is argued that oxygen has very little influence, although in phenetole the cumulative effect of the oxygen and the ethyl group prevents the formation of the compound  $2SbCl_3 \cdot PhOEt$ . Neither anisole nor ethylbenzene forms compounds of this type with antimony tribromide. Nitro-, fluoro-, chloro-, bromo-, and iodo-benzene do not combine with the tribromide at all.

*m*-Dinitrobenzene gives an unstable compound,  $SbCl_3 \cdot C_6H_4(NO_2)_2$ , which, like the compound  $SbCl_3 \cdot PhI$ , does not invariably crystallise out, so that complete f.p. diagrams of these systems are obtainable showing only one eutectic point. The nitro-group diminishes the affinity of the phenyl nucleus for antimony less than the halogens. *p*-Dichloro- and *p*-dibromo-benzene do not combine with antimony trichloride.

*p*-Chlorotoluene gives no compounds, but *o*- and *m*-chlorotoluene give compounds,  $SbCl_3 \cdot C_6H_4MeCl$ , which decompose on melting. No corresponding compounds of antimony tribromide exist.

The three nitrotoluenes form compounds of the formula



the most stable being given by *o*-nitrotoluene, which also combines with antimony tribromide.

Benzene has more affinity for antimony haloids than any of its derivatives, but cyclohexane does not combine at all. The degree of saturation of the phenyl nucleus varies with the nature of the substituting atoms or groups. This variation is not expressible by ordinary structural formulae, but such formulae as have been proposed recently by Kaufmann and by Stark are capable of giving some explanation of it.

The compounds of aniline containing 1, 2, 3, 4, and 6 molecules of aniline per molecule of antimony trichloride are in a class by themselves, and are to be attributed to the residual affinity of the amino group.

R. J. C.

**The Catalytic Action of Mercury in Nitrations.** RICHARD WOLFFENSTEIN and OSKAR BÖTERS (*Ber.*, 1913, 46, 586—589).—Mercury has no catalytic action on the nitration of benzene when concentrated nitric acid or a nitric acid-sulphuric acid mixture is used, nitrobenzene being formed as usual (compare Holdermann, A., 1906, i, 439). When, however, a more dilute nitric acid ( $D=1.31$ ) is used, nitro-phenols are produced. The reaction is first one of oxidation to phenol, and then nitration, since when nitrobenzene is used instead of benzene, no trace of a nitrophenol is produced. Similar reactions take place with toluene, and ethyl- and propyl-benzenes.

To prepare dinitro- or trinitro-phenol, a mixture of benzene (100 grams), nitric acid (800 grams;  $D=1.31$ ), and mercuric nitrate (15 grams) is heated on the water-bath under reflux, stirring vigorously meanwhile. At the end of the reaction, the flask contains a mass of crystals of 2:4-dinitrophenol and of picric acid. Additive mercury compounds are formed as intermediate products.

Instead of using nitric acid, nitrous acid, nitrogen dioxide or tetroxide, and nitrogen pentoxide may be used. For example, a mixture of 120 grams of benzene, 20 grams of mercuric nitrate, and 270 grams of nitrogen tetroxide is kept at the ordinary temperature for a few days, after which a crystalline mass of almost pure 2:4-dinitrophenol is obtained.

T. S. P.

**Hydrogenation of Aromatic Compounds by means of Platinum and Hydrogen. II. Dihydronaphthalene.** RICHARD WILLSTÄTTER and VICTOR L. KING (*Ber.*, 1913, 46, 527—535. Compare Willstätter and Hatt, A., 1912, i, 545).—Dihydronaphthalene has not previously been prepared free from contamination with naphthalene or tetrahydronaphthalene. It may be obtained pure by distilling the quaternary hydroxide of tetrahydro- $\beta$ -naphthylamine in a vacuum, or more conveniently by reducing naphthalene dibromide by means of zinc powder and alcohol at  $60^\circ$ . Pure dihydronaphthalene is a colourless oil with a sweet odour, b. p.  $84.5^\circ/16$  mm.,  $D_4^{20} 0.9974$ ; it crystallises in large plates, m. p.  $-9^\circ$ .

When hydrogenated by means of platinum and hydrogen, the first stage is the formation of tetrahydronaphthalene, the one nucleus only being saturated. The further reduction to a completely saturated perhydronaphthalene takes place very slowly.

Naphthalene under similar conditions yields no tetrahydronaphthalene at any stage of the process, but a mixture of naphthalene and perhydronaphthalene,  $C_{10}H_{16}$ , is always obtained. This behaviour is not in accord with an aromatic-olefinic structure for naphthalene, such as proposed by Willstätter and Waser (A., 1912, i, 18).

F. F. A.

**Derivatives of *p*-Xylene.** JAN J. BLANKSMA (*Chem. Weekblad*, 1913, 10, 136—141. Compare A., 1910, i, 661).—The melting-point curve of mixtures of 2:3-dinitro-*p*-xylene and 2:6-dinitro-*p*-xylene has been plotted, and a number of derivatives of *p*-xylene have been prepared. The curve indicates the formation of an additive product containing equimolecular proportions of the two substances.

Reduction of 2:5-dinitro-*p*-xylene with ammonium sulphide yields



5-nitro-*p*-2 xylidine, m. p. 142°, converted by Sandmeyer's reaction into 2-bromo-5-nitro-*p*-xylene, colourless crystals, m. p. 70°, which is reduced by iron powder and sulphuric acid to 5-bromo-*p*-2-xylidine, colourless crystals, m. p. 96°. Acetic anhydride converts this substance into 5-bromo-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 180°, also formed by the action of a solution of bromine in glacial acetic acid on 2-aceto-*p*-2-xylidide. On saponification it yields 5-bromo-*p*-2-xylidine, already mentioned. On substituting bromine for the amino-group by Sandmeyer's reaction, there is formed 2:5-dibromo-*p*-xylene, m. p. 75°, also produced by bromination of *p*-xylene.

Bromine dissolved in glacial acetic acid transforms 5-nitro-*p*-2-xylidine into 3-bromo-5-nitro-*p*-2-xylidide, pale yellow crystals, m. p. 125°, converted by acetic anhydride and a trace of concentrated sulphuric acid into 3-bromo-5-nitro-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 208°. Replacement of the amino-group in 3-bromo-5-nitro-*p*-2-xylidine produces 2:3-dibromo-5-nitro-*p*-xylene, colourless crystals, m. p. 99°.

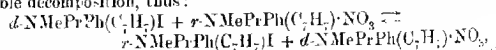
Bromine in glacial acetic acid reacts with *p*-2-xylidine, forming 3:5-dibromo-*p*-2-xylidine, m. p. 65°, converted by diazotisation and the action of boiling alcohol into 2:6-dibromo-*p*-xylene, colourless plates of mother-of-pearl lustre, m. p. 32°, also obtained in an impure liquid form by the bromination of *p*-xylene. Nitration in presence of sulphuric acid converts 2:6-dibromo-*p*-xylene into 2:6-dibromo-3:5-dinitro-*p*-xylene, colourless crystals, m. p. 190°.

3:5-Dibromo-*p*-2-xylidine is converted by acetic anhydride and concentrated sulphuric acid into 3:5-dibromo-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 192° (not 165°, as stated in *Rec. trav. chim.*, 1906, 25, 362). This substance is transformed by nitric and sulphuric acid into 3:5-dibromo-6-nitro-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 256°, which is hydrolysed to 3:5-dibromo-6-nitro-*p*-2-xylidine, yellow crystals, m. p. 176°, also formed by bromination of 6-nitro-*p*-2-xylidine. By diazotisation and the action of boiling alcohol, this substance yields 3:5-dibromo-2-nitro-*p*-xylene, colourless crystals, m. p. 85°, which is converted by nitric and sulphuric acid into 3:5-dibromo-2:6-dinitro-*p*-xylene, already mentioned.

Replacement of the amino-group in 6-nitro-*p*-2-xylidine by bromine by the Sandmeyer reaction produces 2-bromo-6-nitro-*p*-xylene, pale yellow crystals, m. p. 38°.

A. J. W.

Kinetics of Ammonium Salts. EDGAR WEDERKIND and F. PASCHKE (*Zeitsch. physikal. Chem.*, 1913, 82, 314—324).—Polenical, an answer to von Halban (*A.*, 1911, i, 852; compare also *A.*, 1909, ii, 722; 1908, i, 723; 1911, i, 628). Several new preliminary experiments are given. It is shown that the addition of an inactive non-decomposable salt to a chloroform solution of an active iodide does not decrease the dissociation of the active iodide, but brings about a double decomposition, thus:



and of these four substances the iodides alone can dissociate, so that the decrease in the rate of dissociation, which is determined potenti-

metrically, is explained. The remaining and unchangeable activity is due to the active nitrate which exists together with inactive nitrate in the solution. The latter can be precipitated by ether, and the amount of active nitrate determined, which is always found to be equal in concentration to that of the inactive nitrate added. Preliminary experiments are given on the rate of formation of phenylbenzylmethylpropylammonium bromide in chloroform solution at various temperatures from methylpropylaniline and benzyl bromide. J. F. S.

**The Kinetics of Ammonium Salts.** HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1913, **82**, 510—512).—Polenical, an answer to Wedekind and Paschke's criticism (preceding abstract) of Halban's paper (*A.*, 1911, i, 852). J. F. S.

**Nitro derivatives of Cresyl Oxides [Tolyl Ethers].** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], **13**, 169—173).—Most of this work has been published already (this vol., i, 173, 261). *p*-Tolyl ether on nitration yields only a *tetranitro* derivative, m. p. 84°, crystallising in yellow needles, and furnishing on boiling with a dilute solution of potassium hydroxide an amorphous, red powder which does not melt at 390°. T. A. II.

**Nitro derivatives of Cresylene Oxides [Tolylene Oxides].** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], **13**, 173—176). Compare this vol., i, 261).—Part of this work has been published already (*loc. cit.*). *p*-Tolylene oxide, m. p. 166°, on nitration in acetic acid solution at 80° yields a mixture of the *mono*- and *dinitro*-derivatives. The former has m. p. 197°, and is sparingly soluble in boiling alcohol. The dinitro-derivative has m. p. 136°, and is readily soluble in boiling alcohol; it alone is formed when the nitration is effected in sulphuric acid solution in the cold. No higher nitro-derivative of the para-ether could be obtained, whence the author considers that the union of the two nuclei is in the ortho-position to the ether linking, whilst in *o*-tolylene oxide (*loc. cit.*) it is in the meta-position. T. A. II.

**Preparation of Halogenated Aminonaphtholsulphonic Acids.** FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.P. 254715).—Substituted aminonaphtholsulphonic acids can be readily prepared by the halogenation of the *ON*-diacyl derivatives of 2-aminonaphtholsulphonic acids with subsequent elimination of the acyl groups. 5-Chloro-6-amino-1-naphthol-3-sulphonic acid crystallises from water as a colourless powder. 5-Bromo-di-*p*-tolylsulphonyl-6-amino-1-naphthol-3-sulphonic acid is a yellow, crystalline powder. The preparation of 5-bromo-6-amino-1-naphthol-3-sulphonic acid is also described. F. M. G. M.

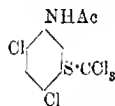
**3-Aminophenyl Mercaptan.** THEODOR ZINCKE and JOH. MÜLLER (*Ber.*, 1913, **46**, 775—786).—The preparation of 3-aminophenyl mercaptan and of 3-aminophenyl methyl sulphide is described. A number of derivatives of the latter have been investigated.

*Acetylcholine-m-sulphonyl chloride*,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , is formed by

the action of phosphorus pentachloride on the corresponding sodium salt. It forms white needles, m. p. 88°, and is readily converted into the *amide*, m. p. 217°, and the *anilide*, m. p. 179°. Reduction of an alcoholic solution of the chloride by means of zinc dust transforms it into 3:3'-diacetylaminodiphenyl disulphide,  $S_2(C_6H_4 \cdot NHAc)_2$ , m. p. 210°, from which 3:3'-diaminodiphenyl disulphide, colourless needles, m. p. 52°, is obtained by hydrolysis. The corresponding *hydrochloride* dissolves freely in water, whilst the *nitrate* and *sulphate* are sparingly soluble. When an alcoholic solution of the hydrochloride is boiled with sodium sulphide in the presence of a small quantity of sodium hydroxide, 3-aminophenyl mercaptan, b. p. 180—190°/16 mm., is formed as a pale yellow oil, which, when pure, is fairly stable towards air, but is readily oxidised when impure. Ferric chloride converts it into the disulphide. The *hydrochloride* and *sulphate* were examined. It forms a *diacetyl* derivative, m. p. 97°. With alcoholic benzaldehyde, it yields a *benzylidene* derivative,  $CHPh(S \cdot C_6H_4 \cdot N : CHPh)_2$ , yellow powder, m. p. 59° (compare A., 1912, i, 257).

3-Acetylaminophenyl methyl sulphide,  $NHAc \cdot C_6H_4 \cdot SMe$ , needles, m. p. 75°, is obtained by reducing 3:3'-diacetylaminodiphenyl disulphide in alcoholic solution by means of sodium sulphide in the presence of sodium hydroxide and treatment of the product so obtained with methyl sulphate. Bromine converts it into a *perbromide*, which is

readily transformed into a dibromo-substitution *product*. When a solution of it in chloroform is cooled in ice and saturated with chlorine, a pentachloro-compound, needles, m. p. 160°, probably having annexed formula, is obtained, which, when heated with aniline, yields triphenylguanidine and *dichloro-3-acetylaminophenyl mercaptan*, m. p. 152°. Hydrolysis of



3-acetylaminophenyl methyl sulphide by means of hydrochloric acid in aqueous alcoholic solution yields the *hydrochloride* of 3-aminophenyl methyl sulphide, from which the free *base*, pale yellow oil, b. p. 163—165°/16 mm., is obtained by means of ammonia. The *sulphate* was examined.

3-Methylthiophenyltrimethylammonium iodide,  $SMe \cdot C_6H_4 \cdot NMe_3^+ I^-$ , m. p. 183—185° (decomp.), is obtained by the action of excess of methyl iodide on a methyl-alcoholic solution of 3-acetylaminophenyl methyl sulphide. It forms a di-iodo- and a tetra-iodo-additive product. The free *base* is obtained by evaporation of its solution in a vacuum as yellowish-white, hygroscopic crystals.

3-Methylthiophenyltrimethylammonium chloride, obtained from the corresponding iodo and silver chloride, forms white, hygroscopic needles. It yields a pale yellow, stable *platinichloride*, and an orange-yellow *dichromate*.

3-Dimethylaminophenyl methyl sulphide, pale yellow oil, b. p. 165—167°/16 mm., is obtained when the above iodide is heated above its m. p. under diminished pressure. It forms a readily soluble *hydrochloride* and *sulphate*.

3-Acetylaminophenyl methyl sulphide is oxidised by hydrogen peroxide in glacial acetic acid solution to the corresponding *sulphoxide*,  $NHAc \cdot C_6H_4 \cdot SO \cdot CH_3$ , needles, m. p. 112°; this is converted by

hydrogen bromide into a *perbromide*, which readily passes into a mono-bromo-substitution *product*. When heated with aqueous alcoholic potassium hydroxide the above acetyl derivative is transformed into 3-aminophenylmethylsulphoxide, colourless, rhombic leaflets, m. p. 115°. The *hydrochloride*, white needles, is readily soluble in water.

3-Acetylaminophenylmethylsulphone,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Me}$ , obtained by the action of a larger quantity of hydrogen peroxide on a solution of 3-acetylaminophenyl methyl sulphide in glacial acetic acid (compare above), forms small, white needles, m. p. 137°, and is converted by aqueous alcoholic hydrogen chloride into 3-aminophenylmethylsulphone, m. p. 72°.

3-Methylthiolbenzenediazonium chloride,  $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl}$ , is obtained in moderately stable, yellow leaflets by the addition of amyl nitrite to an alcoholic solution of the hydrochloride of 3-aminophenyl methyl sulphide in the presence of alcoholic hydrogen chloride. It couples with dimethylaniline and with  $\beta$ -naphthol, yielding dyes which crystallise in red needles. It decomposes when heated with water, but a phenol could not be isolated from the product of the reaction. It was transformed by the usual methods into 3-methylthiolbenzonitrile, white needles, m. p. 40° (3-methylthiolbenzoic acid, leaflets, has m. p. 129°), and 3-methylthiolphenyl iodide, almost colourless oil, b. p. 157°/16 mm.

3:3'-Diacetylaminodiphenyl disulphide is converted into the corresponding ammonium iodide,  $\text{S}_2(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , m. p. 185–186° (decomp.), when heated with methyl alcohol and methyl iodide; this substance, when heated under diminished pressure, yields 3:3'-dimethylaminodiphenyl disulphide,  $\text{S}_2(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , colourless oil, b. p. 162–166°/16 mm. A solution of the latter in formic acid is converted by amyl nitrite in the presence of a little hydrochloric acid into 6:6'-dinitroso-3:3'-dimethylaminodiphenyl disulphide,

$\text{S}_2(\text{C}_6\text{H}_3[\text{NO}] \cdot \text{NMe}_2)_2$ , dark green needles, m. p. 130°, which is reduced by hydrogen sulphide in ammoniacal solution to 6-amino-2-dimethylaminophenyl mercaptan. The *hydrochloride* of the latter, white needles, m. p. 235° (decomp.), was investigated. It forms a colourless double salt with mercuric chloride. With potassium ferricyanide, it yields a dark green precipitate, the colour of which deepens on addition of alkali. Ferric chloride converts it into a dark red oxidation product, which yields a dark violet double salt with mercuric chloride. Hydrogen sulphide decomposes the latter, the original mercaptan being regenerated.

H. W.

**Basic Properties of Sulphoxides and their Position Among the Organo-metallic Bases.** EMIL FROMM (*Annalen*, 1913, 396, 75–103).—The similarities in behaviour between bases of the type  $\text{R}_n \cdot \text{Md} \cdot \text{OH}$  (where Md represents a metalloid element such as N, P, As, Sb, O, S, Se, Te, or I, and  $n$  the number of atoms of hydrogen with which it can unite, and R an organic radicle) have frequently been emphasised. Compounds of the type  $\text{MdR}_n$  may be regarded as the anhydrides of  $\text{R}_{n+1}\text{Md} \cdot \text{OH}$ . All these bases are monacidic.

The anhydrides,  $R_nMdO$ , of a second series of bases of the type  $R_nMd(OH)_2$  are known. In the anhydrides, Md may be any one of the elements given above, but in the hydroxides hitherto Md has been only N, P, As, Sb, or Te. All these bases and their anhydrides are diacidic, and the anhydrides or their salts are characterised by the three equilibrium reactions: (i)  $R_nMdO \rightleftharpoons R_nMd + O$ ; (ii)  $R_nMdX \rightleftharpoons R_nMd + X_2$  (where X is halogen); (iii)  $R_nMdCl_2 + H_2O \rightleftharpoons R_nMdCl \cdot OH + HCl \rightleftharpoons R_nMdO + 2HCl$ .

In the present communication the author deals with substances in which Md is sulphur, and, therefore,  $n=2$ . Sulphoxides can be prepared by reaction (i), the oxygen being supplied by nitric acid, hydrogen peroxide, or chromic acid, and also by reactions (ii) and (iii). The dichlorides of diaryl sulphides have been prepared by Fries and Vogt (A., 1911, i. 538), and are converted into sulphoxides by water; di-iodides of dialkyl sulphides, which have long been known, are, it is now shown, converted into sulphoxides by silver acetate.

It is also shown that sulphoxides can combine with one equivalent of hydrogen chloride to form hydrogen salts,  $OH \cdot SR_2Cl$ , and with two equivalents of hydrogen bromide or iodide to form normal salts,  $R_2SX_n$ , which are identical with the dibromides or di-iodides produced by reaction (ii). The hydrogen salts and the normal salts are both hydrolysed more or less rapidly by water, reproducing the sulphoxide. In addition to hydrolysis, the normal salts can also dissociate according to reaction (i), and it depends on the relative velocities of dissociation and of hydrolysis whether a normal salt yields the sulphoxide or the sulphide by treatment with aqueous alkali hydroxide or silver acetate. The parent substance,  $H_2SO$ , of the sulphoxides, and its tautomeric form,  $HS \cdot OH$ , are unknown; anthraquinone derivatives of both have been described by Fries (A., 1912, i. 1005).

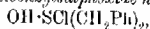
The relations between disulphides and disulphoxides and the basic properties of the latter can be represented by equations similar to (i), (ii), and (iii).

[With FRITZ SCHÄFFER, AQUILA FORSTER, and DOMS VON SCHIEBSCHEWITZKI.]—*o*-Nitrophenyl benzyl sulphide and the para-isomeride, 2:4-dinitrophenyl benzyl sulphide, dinitrophenyl methyl sulphide, and *s*-di-*o*-nitrophenylthioethane, resemble di-*p*-tolyl sulphide (Fromm and Raiziss, A., 1910, i. 534) in not forming additive compounds with bromine; 2:4-dinitrophenyl benzyl sulphide in cold chloroform yields *bromodinitrophenyl benzyl sulphide*,  $C_6H_4Br(NO_2)_2 \cdot S \cdot CH_2Ph$ , m. p. 104°, yellow needles. Also the dibromides cannot be obtained from the sulphoxides and hydrogen bromide. Both reactions proceed, however, when the nitro-groups are reduced to amino-groups and the latter acetylated; thus di-*o*-acetylaminophenylthioethane and bromine in cold chloroform yield the *tetrabromide*,  $C_6H_4(SBr \cdot C_6H_4 \cdot NHAc)_2$ , m. p. 60–61°, unstable, orange crystals, which is converted by water into di-*o*-acetylaminophenylsulphoxyethane,  $C_6H_4(SO \cdot C_6H_4 \cdot NHAc)_2$ , m. p. 214°, colourless needles; the latter and hydrogen bromide in chloroform regenerate the tetrabromide.

Dibenzyl sulphide and chlorine in petroleum at 6° yield the very unstable *dichloride*,  $SCl_2(C_6H_5)_2$ , which is converted into the sulphoxide by water. The dibromide is more stable (Fromm and

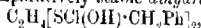
Reiziss, *loc. cit.*). The *di-iodide*,  $\text{SI}_2(\text{CH}_2\text{Ph})_2$ , m. p. 64–65°, violet crystals, prepared from the sulphide and iodine in glacial acetic acid on the water-bath, is extremely stable. It is decomposed, without hydrolysis, by dilute sodium hydroxide, dibenzyl sulphide being regenerated; the hydrolysis is effected by silver acetate in dilute acetic acid, whereby dibenzylsulphoxide is produced.

Dibenzylsulphoxide and hydrogen iodide in chloroform at 0° yield the preceding dibenzyl sulphide di-iodide. The sulphoxide and hydrogen chloride in benzene form *dibenzylsulphoxide hydrochloride*,



m. p. 90°, colourless crystals, which does not further react with hydrogen chloride, and is decomposed into the sulphoxide by water or in a vacuum.

*p*-Dibenzylthioethane reacts with chlorine in cold petroleum to form the unstable *tetrachloride*,  $\text{C}_6\text{H}_4(\text{SCl}_2\text{CH}_2\text{Ph})_2$ , white crystals, with bromine in cold chloroform to form the moderately stable *tetrabromide*, m. p. 84°, orange-red crystals, and with iodine in boiling glacial acetic acid to form the *tetraiodide*, m. p. 94°, red needles. The tetrachloride and the tetrabromide are very rapidly converted into the disulphoxide by water. On the contrary, the disulphoxide suspended in cold petroleum or chloroform is converted into the tetrabromide by hydrogen bromide, and into a comparatively stable *dihydrochloride*,



by hydrogen chloride.

*p*-Tolyl benzyl sulphide,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{S} \cdot \text{CH}_2\text{Ph}$ , m. p. 44°, prepared from *p*-tolyl mercaptan and benzyl chloride, yields the *sulphoxide*, m. p. 136–137°, by oxidation with 30% hydrogen peroxide in glacial acetic acid or with nitric acid, and reacts with chlorine or bromine in cold petroleum to form respectively the very unstable *dichloride*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{S} \cdot \text{SCl}_2 \cdot \text{CH}_2\text{Ph}$ , and comparatively unstable *dibromide*, and with iodine in hot glacial acetic acid to form the stable *di-iodide*, m. p. 72°, dark blue plates. The dichloride and the dibromide by treatment with water, and the di-iodide by treatment with silver acetate, are converted into *p*-tolylbenzylsulphoxide; the di-iodide and aqueous sodium hydroxide yield *p*-tolyl benzyl sulphide. The dibromide and the di-iodide are obtained from the sulphoxide and hydrogen bromide or iodide in chloroform. *p*-Tolyl methyl sulphide di-iodide,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{S} \cdot \text{MeI}_2$ , m. p. 40°, prepared from its components in petroleum, crystallises in dark blue needles.

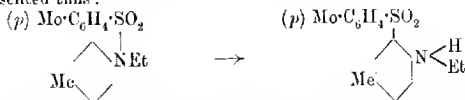
Formaldehyde-*p*-tolylmercaptan (this vol., i, 176) forms a *tetraiodide*,  $\text{CH}_2(\text{SI}_2\text{C}_6\text{H}_4\text{Me})_2$ , m. p. 68–70°, which can also be obtained from the disulphoxide and hydrogen iodide in chloroform, and is not converted into the disulphoxide by silver acetate. Formaldehydebenzylmercaptan also forms a *tetraiodide*,  $\text{CH}_2(\text{SI}_2\text{CH}_2\text{Ph})_2$ , decomp. 110–110°, which is converted by silver acetate, not into the sulphoxide as usual, but into formaldehydebenzylmercaptan.

In boiling glacial acetic acid, benzyl disulphide and iodine form the *tetraiodide*,  $\text{S}_2(\text{CH}_2\text{Ph})_4$ , decomp. 113–120°, green crystals, which is converted into the disulphoxide by silver acetate in hot glacial acetic acid; from the latter the tetraiodide is regenerated by hydrogen iodide at –5° in carbon tetrachloride. *Benzyl disulphide tetrachloride* is

extremely unstable, and the *tetrabromide* has m. p.  $2^{\circ}$  (decomp.); the latter and silver acetate yield the disulphoxide. C. S.

**Substituted Aryl Sulphonamides.** OTTO N. WITT and D. UERMÉNYI (*Ber.*, 1913, 46, 296–308).—Hinsberg's method for the preparation of secondary bases (A., 1891, 49) has not yet received general application, owing to the difficulty which has been experienced in hydrolysing the sulphonamides. For this purpose Schroeter and Eisleb (A., 1909, i, 575) dissolved the substances in cold concentrated sulphuric acid, but obtained in the case of benzenesulphonanilide, not aniline but sulphanilic acid. It is now shown that good results may be obtained with 80% sulphuric acid. The toluene-*p*-sulphonamide is suspended in this acid and heated to  $135$ – $150^{\circ}$ , when solution and hydrolysis take place. On cooling, *p*-toluenesulphonic acid separates, and is removed by filtration, whilst the base is liberated from the diluted filtrate and distilled in steam. The yields are somewhat impoverished by the formation of non-volatile by-products, which occur to a preponderating extent in the case of ethyl-*p*-toluidine, and consist of a sulphone, being due to the displacement of the *p*-toluenesulphonic acid residue into the ring.

Toluene-*p*-sulphon-*p*-toluidide and also its acetyl derivative, m. p.  $133.5^{\circ}$ , give *p*-toluidine-*m*-sulphonic acid with concentrated sulphuric acid, but sulphonation of the base does not occur with 80% acid at  $150^{\circ}$ . Crude methyl- and ethyl-aniline and also methyl-*o*-toluidine (toluene-*p*-sulphon-methyl-*o*-toluidide,  $C_{12}H_{17}O_2NS$ , has m. p.  $119$ – $120^{\circ}$ ) may be conveniently purified by this process. Toluene-*p*-sulphonethyl-*o*-toluidide,  $C_{16}H_{21}O_2NS$ , forms long needles, m. p.  $75^{\circ}$ , but the ethyl-*o*-toluidine is accompanied by a small quantity of the rearranged sulphone, white needles, m. p.  $134^{\circ}$ . The hydrolysis of toluene-*p*-sulphonethyl-*p*-toluidide, colourless needles, m. p.  $71$ – $72^{\circ}$ , gives less than a 50% yield of ethyl-*p*-toluidine, the chief product being precipitated on adding water, in colourless needles, m. p.  $113^{\circ}$ . It is formed in still greater quantity when concentrated acid is used, and is a secondary base, since it gives an acetyl compound,  $C_{16}H_{23}O_2NS \cdot C_2H_5O$ , in silky, white needles, m. p.  $143$ – $144^{\circ}$ . When the base is heated at  $275^{\circ}$  in a current of hydrogen chloride, ethyl chloride is removed and the resulting primary aminoditolylsulphone,  $C_{14}H_{17}O_2NS$ , colourless crystals, m. p.  $169^{\circ}$ , may be diazotised and deprived of the amino-group. The resulting compound forms colourless needles, m. p.  $116^{\circ}$ , and can be synthesised by condensing the chloride of *m*-toluenesulphonic acid with toluene by means of aluminium chloride. It is, therefore, mp-ditolylsulphone, and the rearrangement of the sulphonamide into a sulphone is to be represented thus:



The sulphone may be nitrated in the cold, and the mononitro-derivative, intensely yellow needles, m. p.  $161^{\circ}$ , forms an acetyl compound,  $NO_2 \cdot C_{16}H_{17}O_2NS \cdot C_2H_5O$ , in colourless crystals, m. p.  $159$ – $160^{\circ}$ . J. C. W.

**Preparation of *p*-Alkyloxyphenylaminoalkyl Sulphites.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 255305).—When acetaldehyde (or its higher homologues) is condensed with *p*-alkyloxyaminobenzenes in the presence of an alkali (or ammonium) hydrogen sulphite it furnishes salts of therapeutic value, and having the general formula  $OR^1 \text{—} \langle \text{C}_6\text{H}_4 \rangle \text{—} NH \cdot CHR \cdot O \cdot SO_2 M$ , where *M* is an alkali metal or ammonium, *R*—methyl or ethyl, and *R*<sup>1</sup> an alkyl group.

*Sodium p-phenetidinethioethyl sulphite*, needles, is obtained when a cooled aqueous solution of 40% sodium hydrogen sulphite (110 parts) is treated with acetaldehyde (20 parts) and *p*-phenetidine (55 parts), and subsequently gently heated until a clear solution is obtained; on cooling, the solution sets to a crystalline mass.

The *p*-phenetidine can be replaced by *p*-anisidine, and the acetaldehyde by propaldehyde.

F. M. G. M.

**Preparation of Aromatic Amino-alcohols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254438).—The reduction of aromatic ketones to the corresponding alcohols has previously been described, and is now found to proceed quantitatively if hydrogen is employed in the presence of colloidal metals of the platinum group.

$OMe \text{—} \langle \text{C}_6\text{H}_4 \rangle \text{—} CH(OH) \cdot CHMe \cdot NH_2$   
 $OMe$

3:4-Dimethoxyphenyl-*α*-propanolamine (annexed formula), hard, colourless crystals, m. p. 138°, is obtained when 100 parts of *α*-aminopropionylveratrole (A., 1910, i, 313) in 300 parts of water with palladous chloride (5 parts), gum arabic (10 parts), and hydrazine hydrate are submitted to the action of hydrogen during two days at 20° and under a pressure of 1.5 atmospheres; the *hydrochloride*, colourless leaflets, has m. p. 212°; whilst the reduction in a similar manner of 4-*α*-aminopropionylcat-*chol* (A., 1910, i, 313) gives rise to a 95% yield of 3:4-dihydroxyphenyl-*α*-propanolamine (annexed formula), m. p. 188°; the *hydrochloride*, a colourless powder, has m. p. 95°.

F. M. G. M.

**Preparation of Esters of Nitroanthraquinonylanthranilic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254475).—When nitroaminoanthraquinones are treated with the esters of *o*-halogenated benzoic acids in the presence of copper (or a salt of copper), they give rise to nitroanthraquinonylanthranilic acid esters.

*Methyl 1-nitro-1-anthraquinonylanthranilate*, reddish-brown needles, m. p. 234–240°, is thus obtained from 1-nitro-1-aminoanthraquinone and methyl *o*-chlorobenzoate. On hydrolysis and subsequent reduction, these compounds furnish the corresponding aminoanthraquinonylanthranilic acids, which are of technical value.

F. M. G. M.

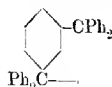
**Metaquinonoids.** OTTO STARK and O. GARBEN (*Ber.*, 1913, 46, 659–666).—The method by which Thiele and Balhorn obtained yellow

VOL. CIV. i.

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tetraphenyl-*p*-xylene from methyl terephthalate (A., 1901, i, 491) has been applied to methyl isophthalate, and a yellow tetraphenyl-*m*-xylene of the annexed formula has been prepared.



*Tetraphenyl-m-xylene glycol*,  $C_{22}H_{26}O_2$ , is obtained by the action of magnesium phenyl bromide on methyl isophthalate in a boiling mixture of benzene and anisole. It crystallises from glacial acetic acid with one molecule of the solvent in light yellow prisms, m. p.  $88^\circ$ , and from light petroleum in the free state, m. p.  $112-113^\circ$ . Hydrogen chloride precipitates from an acetic acid solution the *dichloride*,  $C_{22}H_{24}Cl_2$ , which crystallises from petroleum in white needles, m. p.  $137^\circ$ , and like the *dibromide*, m. p.  $167-168^\circ$ , can be titrated with alkali in alcoholic solution. When heated with zinc dust and Devarda's alloy in benzene (compare Schmidlin, A., 1908, i, 150), a golden-yellow solution with red fluorescence is obtained, from which petroleum precipitates *tetraphenyl-m-xylene*, in yellow needles, m. p.  $210-220^\circ$  (decomp.). It gives the above dichloride with chlorine, but is stable towards oxygen.

When hydrogen chloride is passed into the acetic acid mother liquors of the glycol, a *dichloride* is obtained, which is insoluble in hot petroleum, and has m. p.  $236-238^\circ$ . It may be hydrolysed and converted into a *dimethyl ether*,  $C_{24}H_{30}O_2$ , m. p.  $187-188^\circ$ , from which the *dibromide*, m. p.  $242^\circ$ , is obtained. It is supposed that the  $-C(OH)Ph_2$  group has wandered into the *para*-position and that the compounds are isomeric, according to Schmidlin's isomerism (A., 1912, i, 32), with tetraphenyl-*p*-xylene glycol dimethyl ether, m. p.  $181-182.5^\circ$ , and tetraphenyl-*p*-xylene dibromide, m. p.  $270-272^\circ$  (Thiele and Balhorn, *loc. cit.*). J. C. W.

**Direct Hydrogenation of the Phenylacetic Esters.** Preparation of *cyclohexylacetic Acid*. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, 156, 424-427. Compare A., 1912, i, 353).—The esters of phenylacetic acid are readily hydrogenated by excess of hydrogen in the presence of very active nickel at  $180^\circ$ . By this means the following esters have been prepared.

*Methyl cyclohexylacetate*, b. p.  $200-202^\circ$  (corr.),  $D_4^{20}$  0.9961,  $D_4^{25}$  0.9896,  $n_D^{20}$  1.459. *Ethyl cyclohexylacetate*, b. p.  $211-212^\circ$  (corr.),  $D_4^{20}$  0.9826,  $D_4^{25}$  0.9537,  $n_D^{20}$  1.451 (compare Freundler, A., 1905, i, 890). *Propyl cyclohexylacetate*, b. p.  $228-229^\circ$  (corr.),  $D_4^{20}$  0.9560,  $D_4^{25}$  0.9431,  $n_D^{20}$  1.450. *isoButyl cyclohexylacetate*, b. p.  $240-241^\circ$  (corr.),  $D_4^{20}$  0.9445,  $D_4^{25}$  0.9307,  $n_D^{20}$  1.452. *isoAmyl cyclohexylacetate*, b. p.  $250-251^\circ$  (corr.),  $D_4^{20}$  0.9388,  $D_4^{25}$  0.9267,  $n_D^{20}$  1.454.

The refractive indices are practically constant throughout, but the density diminishes regularly with increase in molecular weight. All these esters are readily saponified by alcoholic potassium hydroxide, giving the free acid, m. p.  $32^\circ$ .

The propylpropionic esters undergo similar hydrogenation.

It is of interest to note that benzyl acetate, the isomeride of methyl phenylacetate, submitted to similar hydrogenation is decomposed, giving

toluene and acetic acid, at the same time destroying the activity of the nickel.

W. G.

**Esters of Cellulose with Benzoic Acid and its Derivatives.** OTTO HAUSER and H. MESCHNER (*Zeitsch. angew. Chem.*, 1913, 26, 137—139).—In the preparation of the esters the authors used hydrocellulose, which was made according to the method of Girard. The hydrocellulose is treated, under cooling, with a large excess of benzoyl chloride and sodium hydroxide, and the resulting product washed with hot water to remove alkali, and finally with alcohol and ether. The results show that the product obtained is always cellulose monobenzoate; no dibenzoate is formed, whatever may be the concentration of the sodium hydroxide (compare Cross and Bevan, A., 1901, i, 452). The only effect of the concentration of the sodium hydroxide is on the time of reaction, the stronger the alkali the shorter the time. The best concentration is 20%, and the temperature should be kept at 20° by appropriate cooling.

*Cellulose mono-p-chlorobenzoate*,  $C_{13}H_{13}O_{11}Cl$ , was prepared similarly from hydrocellulose and *p*-chlorobenzoyl chloride. It is an amorphous, white powder, insoluble in all solvents, non-hygroscopic and non-fusible. Esters could not be obtained from *m*-nitrobenzoyl chloride and *p*-bromobenzoyl chloride, owing to the fact that the high temperature necessary to melt the chloride resulted in its saponification by the sodium hydroxide before the cellulose entered into reaction. *p*-Toluenoyl chloride gave a product corresponding with the formula  $C_{15}H_{26}O_{11}$ , instead of the expected formula  $C_{21}H_{26}O_{11}$ . T. S. P.

**An Interesting Case of Dimorphism.** ALEXIS DUFROIR (*Compt. rend.*, 1913, 156, 473—475).—Vanillyl benzoate is obtained in two distinct crystalline forms, monoclinic or triclinic, accordingly as it is prepared by the hydrogenation of vanillin benzoate in the cold in the presence of platinum black (compare Vavon, A., 1912, i, 260), or by the condensation of benzoyl chloride and sodium vanillyloxide. These two forms are both stable at the ordinary temperature, having been kept for a year unaltered. The triclinic crystals

[ $a:b:c=0.8697:1:0.5283$ ;  $\alpha=90^{\circ}20'$ ;  $\beta=72^{\circ}22'$ ;  $\gamma=72^{\circ}44'$ ] have *m. p.* 99°, whilst the monoclinic

[ $a:b:c=0.7814:1:1.3460$ ;  $\beta=111^{\circ}3'$ ],

observed under a microscope, begin to melt at 96°, and in the liquid obtained, triclinic crystals begin to form, transforming the whole into a friable mass only melting at 99°. This transformation of the monoclinic into the triclinic form when the two are in contact is retarded by diminution in temperature and becomes inappreciable at 30°.

W. G.

**Nitration of Benzoic Acid in the Presence of Mercury** RICHARD WOLFFENSTEIN and W. PAAR (*Ber.*, 1913, 46, 589—599).—When benzoic acid (50 grams) is nitrated with nitric acid (300 grams;  $D=1.35$ ) in the presence of mercuric nitrate, 2:4:6-trinitro-*m*-hydroxybenzoic acid is obtained. The mixture is heated on the brine-bath at

105° for twenty hours, after which it is filtered from unchanged benzoic acid, the filtrate made alkaline to remove the mercury, acidified, and then extracted with ether to dissolve out any *m*-nitrobenzoic acid formed. The aqueous solution is then concentrated in order to obtain crystals of the readily soluble 2:4:6-trinitro-*m*-hydroxybenzoic acid. Various trinitrohydroxybenzoic acids have been described in the literature, and in order to compare them with the above acid they have been again prepared by the authors. Shardingier (A., 1876, 584) obtained an acid by the nitration of anthraflavone. Since anthraflavone is a mixture of the two isomerides, anthraflavic acid and 1:7-dihydroxy-anthraquinone, the authors have nitrated each of these substances. In each case a tetranitro-derivative is first obtained, which undergoes fission, on further action of nitric acid, with the formation of the above-mentioned 2:4:6-trinitro-*m*-hydroxybenzoic acid. The third isomeride of anthraflavic acid is anthrarufin, the tetranitro-derivative of which has been prepared by Liebermann (A., 1879, 537). This on boiling with nitric acid undergoes fission with the formation of the above acid. Tetranitroanthrarufin is therefore 3:4:6:8-tetranitro-1:5-dihydroxyanthraquinone. Beilstein and Geitner (*Annalen*, 1866, 139, 12) obtained a trinitrohydroxy-acid by the action of fuming nitric acid on *m*-aminobenzoic acid, and this the authors prove to be identical with their acid.

2:4:6-Trinitro-*m*-hydroxybenzoic acid,  $C_7H_3O_9N_3$ , crystallises with one molecule of water of crystallisation, in rhombic tablets; *m.* p. 180°. It forms a series of salts, characterised by their water of crystallisation. The *sodium*, *potassium*, *barium*, and *silver* salts have  $2H_2O$ , and the *copper* salt,  $5H_2O$ . Its constitution was proved by its conversion into picric acid when heated in small quantities (0.2 gram) at a time at 195°. The simplest method of preparation is from *m*-hydroxybenzoic acid. Five grams of this acid are dissolved in 30 grams of fuming nitric acid ( $D = 1.52$ ), and the solution heated on the water-bath. The nitric acid is expelled on the water-bath, the residue again evaporated down with nitric acid, then with water, and finally extracted with benzene, leaving the pure acid.

T. S. P.

2:4:6-Trinitro-*m*-hydroxybenzoic Acid. RICHARD WOLFFENSTEIN and W. PAAR (*Ber.*, 1913, 46, 680—682. Compare preceding abstract).—E. F. Smith (*Proc. Amer. Phil. Soc.*, 25) described a compound, which he obtained by treating ethyl *m*-hydroxybenzoate with nitrous acid and then with an excess of potassium hydroxide, as a trinitro-*m*-hydroxybenzoic acid, basing his formula on an estimation of potassium in the monopotassium salt. It might be expected that the hydroxyl hydrogen should also have been replaced by potassium and that the acid might be identical with Wolffenstein and Paar's compound. These authors have repeated Smith's experiment, and find that the product is in reality an ester which cannot be hydrolysed by prolonged boiling with alcoholic or aqueous potash, and is therefore, according to Victor Meyer's rule that ortho-substituents protect a carboxyl or ester group, *ethyl* 2:6-dinitro-*m*-hydroxybenzoate. It has *m.* p. 117°.

J. C. W.

**Action of Hydrogen Cyanide on *p*-Nitrobenzaldehyde.**  
 (GUSTAV HELLER [with OTTO FRITSON] (*Ber.*, 1913, 46, 280—294).  
 —When *p*-nitrobenzaldehyde is suspended in glacial acetic acid and shaken with a concentrated aqueous solution of potassium cyanide until dissolved, it is converted into *p*-nitromandelonitrile, which may be precipitated by water. The behaviour of this substance towards various reagents, its conversion into nitro- and amino-mandelic acid, and attempts to form anhydrides of the latter acid are described.

*p*-Nitromandelonitrile,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}$ , crystallises from benzene in faintly yellow needles, *m. p.* 109—110°, which on hydrolysis with hydrochloric acid readily yield *p*-nitromandelic acid. Towards sodium hydroxide it is very sensitive, and from the product of the reaction, *p*-nitroso-, *p*-nitro-, and *p*-azoxybenzoic acids have been isolated.

*o*-Benzoyloxy-*p*-nitrophenylacetic acid,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OBz})\cdot\text{CO}_2\text{H}$ , is obtained by benzoylating the acid in pyridine solution, in yellowish-white prisms, *m. p.* 185—186°. It is easily hydrolysed, and all attempts to reduce it resulted in the production of benzoic acid. The reduction of *p*-nitromandelic acid itself follows different courses; with zinc and acetic acid it results in *p*-azoxymandelic acid,  $\text{C}_8\text{H}_7\text{O}_2\text{N}_2$ , in yellow needles, which darken at 190°; with stannous chloride the product is *p*-aminophenylacetic acid; ferrous sulphate and ammonia lead to *p*-aminomandelic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , which forms faintly yellow needles from warm water, and a colourless hydrochloride. When warmed for a long time in water, it gradually deposits a yellow anhydride,  $(\text{C}_8\text{H}_7\text{O}_2)_2$ , *m. p.* 210° (decomp.), which is insoluble in organic solvents. *p*-Aminomandelic acid yields a normal benzoyl derivative in sodium carbonate solution as a crystalline powder, *m. p.* 218, which does not lose water when heated with acetic anhydride, but

when benzoylated in pyridine in the cold, the product is 3-hydroxy-1-benzoylindole (annexed formula).

This substance could only be obtained as a colourless, amorphous powder, which was not readily attacked by warm aqueous alkali, but was hydrolysed by cold alcoholic potash to *p*-benzoylamino-mandelic acid.

If the solution of *p*-nitrobenzaldehyde in concentrated potassium cyanide and acetic acid is not immediately precipitated by water, but is left for a day, *pp*-dinitrobenzoylbenzoin cyanide,

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , is deposited. This crystallises in pale yellow needles, *m. p.* 267—268°, cannot be acetylated, and gives no reaction with ferric chloride. On reduction it yields *p*-aminobenzoic acid, and when dissolved in hot sodium hydroxide it deposits *p*-azoxybenzoic acid. When the red solution in cold sodium hydroxide is at once filtered into hydrochloric acid, however, 4-nitro-1-nitrosostilbene- $\alpha$ -*3*-diol,

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NO}$ , can be extracted by means of boiling water from the precipitate. It forms colourless leaflets, *m. p.* 225° (decomp.), which give an intense, dark red colour with ferric chloride, and form acetyl and benzoyl derivatives which could not be obtained pure. J. C. W.

**Preparation of Carboxydiarylhydrols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254122).—6-Hydroxy-2:4-dimethylbenzoic acid, m. p. 66°, is prepared by the action of carbon dioxide on *s*-xlenol; when it is slowly added to a cooled solution of *p* diethylaminobenzaldehyde (1 mol.) in concentrated sulphuric acid, it gives rise to a *hydrol*, which can be further condensed with *o*-hydroxytoluic acid to yield *compounds*, which dye wool in violet shades.

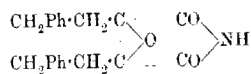
Similar *compounds* are also described from *o*-chloro-*p*-diethylaminobenzaldehyde with *m*-hydroxytoluic acid, and its further condensation with *o*-hydroxytoluic acid; from *o*-chlorobenzaldehyde with 6-hydroxy-2:4-dimethylbenzoic acid, followed by condensation with *o*-hydroxytoluic acid, whilst the tinctorial properties of other similar compounds are tabulated in the original. F. M. G. M.

**Preparation of 2-Halogen-5 acylaminobenzoylbenzoic Acid.** ARTES GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 254091).—

3-Aminobenzoylbenzoic acid (annexed formula) and its homologues can be readily acetylated by ordinary methods, and on subsequent halogenation (in the same solution) yield 2-halogen-5-acetylaminobenzoylbenzoic acid.

The following compounds are described: 6-Bromo-3-acetylaminobenzoylbenzoic acid, hard crystals, m. p. 218°; 6-bromo-3-acetylaminobenzoylbenzoic acid (prepared from 3-amino-*p*-toluylbenzoic acid), colourless needles, m. p. 226°; 2-bromo-5-acetylaminobenzoylbenzoic acid (from 3-amino-4-carboxybenzoylbenzoic acid, m. p. 265°), short, colourless, rod-like crystals, m. p. 264–266°, and 2-chloro-5-*p*-toluenesulphonyl-*p*-toluylbenzoic acid, colourless rods, m. p. 135°. F. M. G. M.

**$\alpha$ -Hydroxy- $\gamma$ -phenylcrotonic Acid.** An Example of an Ether of a Ketone Hydrate. J. BOGGAERT (*Compt. rend.*, 1913, 166, 555–556).—The acid amide,  $C_{20}H_{25}O_5N$ , obtained by the hydrolysis of  $\alpha$ -hydroxy- $\gamma$ -phenylcrotonamide (compare this vol., i, 269) on treatment with potassium permanganate in dilute acid solution gives a *compound*,



$C_{20}H_{25}O_5N$ , m. p. 120°, to which the author assigns the annexed constitution. The

presence of the imide group in the compound is shown (1) by its pseudo-acid properties; (2) by its transformation into an *acid amide*,  $C_{20}H_{25}O_4N$ , m. p. 171°, and finally to the dibasic acid,  $C_{20}H_{25}O_5$ , m. p. 204°, by the action of dilute alkali hydroxides; (3) by the formation of a *N*-methyl derivative, m. p. 86°, which liberates methylamine on treatment with alkali. The compound, unlike the acid amide from which it is prepared (*loc. cit.*), is not readily decomposed by alkalis to give benzylpyruvic acid. Its preparation by the elimination of two tertiary hydroxyl groups appears to be the reverse of Wagner's action. W. G.

**Preparation of Esters of Acetylsalicylic [*o*-Acetoxybenzoic] Acid.** RICHARD WOLFFENSTEIN and JOSEF ZELTNER (*Ber.*, 1913, 46, 382—386).—Attempts to prepare ethyl *o*-acetoxybenzoate by the action of *o*-acetoxybenzoyl chloride on ethyl alcohol led to the isolation of ethyl salicylate, ethyl acetate, salicylic acid, and salicylic anhydride, the primarily formed ethyl *o*-acetoxybenzoate being decomposed by the hydrogen chloride liberated during the reactions. Satisfactory results were, however, obtained when the reaction was carried out in the presence of a substance capable of absorbing hydrogen chloride, for example, quinoline.

*Trichloroisopropyl o-acetoxybenzoate* was obtained by heating a mixture of *o*-acetoxybenzoyl chloride, trichloroisopropyl alcohol, and dimethylaniline on the water-bath during two hours. It had m. p. about 65°, and could not be distilled without decomposition. Occasionally this ester was obtained in an oily form, which could not be caused to crystallise, but which, according to analysis, was pure.

*Trichloro-tert.-butyl o-acetoxybenzoate*, m. p. 55—57°, after previous softening, b. p. about 180°/16 mm. (slight decomp.), was obtained by heating *o*-acetoxybenzoyl chloride and *tert*-trichlorobutyl alcohol at 140° in the presence of barium carbonate. II. W.

**Preparation of Chloroanthraquinonecarboxylic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P., 255121).—The method previously described (*A.*, 1911, i, 466), in which anthraquinone was chlorinated in sulphuric acid solution in the presence of iodine, has now been extended to the anthraquinone- $\alpha$ - and  $\beta$ -carboxylic acids.

When anthraquinone- $\beta$ -carboxylic acid dissolved in fuming sulphuric acid (in the presence of iodine) is chlorinated at 125°, it gives rise to a *dichloroanthraquinonecarboxylic acid*, yellow crystals, m. p. above 300°, which when heated with *p*-toluidine furnishes an intensely green quinazolin-like derivative, thus indicating that the chlorine atoms are in the para-position with regard to each other.

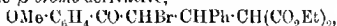
The analogous compound from anthraquinone- $\alpha$ -carboxylic acid crystallises from acetic acid, and has m. p. 210—211°. The anthraquinonedicarboxylic acids can also be employed in this reaction.

F. M. G. M.

**Saturated  $\delta$ -Ketonic Esters and their Derivatives.** DOROTHY A. HAIN and ANGIE G. ALLBEE (*Amer. Chem. J.*, 1913, 49, 171—179).—Kohler (*A.*, 1911, i, 384) has described a general method for the preparation of unsaturated  $\delta$ -ketonic esters; this method has now been applied to the production of the corresponding saturated compounds.

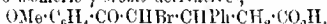
*Ethyl  $\beta$ -anisoyl- $\alpha$ -phenylethylmalonate*,  
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ ,  
 m. p. 78°, obtained by the condensation of ethyl malonate with anisyl styryl ketone in presence of piperidine, crystallises in plates or stout needles. The corresponding *isobutyl* ester, m. p. 104°, forms plates or slender needles. When an alcoholic solution of the ethyl ester is treated with concentrated aqueous solution of potassium hydroxide, the *potassium salt* of  $\beta$ -anisoyl- $\alpha$ -phenylethylmalonic acid separates, which

is converted by acids into the *potassium hydrogen* salt and subsequently into the acid itself. *β-Anisoyl-α-phenylethylmalonic acid*, m. p. 165° (decomp.), crystallises from water in slender needles containing water of crystallisation, which is eliminated below 130°. By the action of bromine on a solution of ethyl *β-anisoyl-α-phenylethylmalonate* in chloroform, the *β-bromo-derivative*,

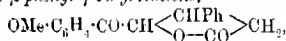


m. p. 97°, is obtained, which forms large, six-sided prisms.

When *β-anisoyl-α-phenylethylmalonic acid* is heated at 165–170° until the evolution of carbon dioxide ceases, *γ-anisoyl-β-phenylbutyric acid*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 152°, is obtained, which crystallises in plates or prisms; its *methyl ester*, m. p. 86°, forms long plates or prisms, and is hydrolysed by potassium hydroxide with formation of the *potassium* salt, which crystallises with  $\text{H}_2\text{O}$ . On the addition of bromine to a solution of *γ-anisoyl-β-phenylbutyric acid* in chloroform, two isomeric *γ-bromo-derivatives*,



are obtained with m. p. 144° (decomp.) and 119° respectively, which both behave in the same way when treated with sodium carbonate, yielding *γ-anisoyl-β-phenyl-γ-butyrolactone*,



m. p. 109°, which forms large, six-sided prisms. The *methyl ester* also yields two *γ-bromo-derivatives*, m. p. 84° and 122°. E. G.

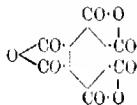
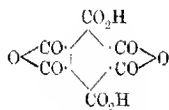
**A New Oxide of Carbon,  $\text{C}_{12}\text{O}_6$ .** HANS MEYER and KARL STEINER (*Ber.*, 1913, 46, 813–815).—When mellitic acid is subjected to the action of dehydrating agents, either it remains unchanged or,

by more drastic treatment, it is converted into the anhydride of pyromellitic acid. As intermediate product, an anhydrocarboxylic acid (annexed formula) appears to be formed. This substance can be isolated in the pure state by prolonged boiling of mellitic acid with thionyl chloride or by heating these substances at 180°

during several hours. It forms a white, crystalline powder, which unites with the calculated quantity of water to form mellitic acid, and which, when strongly heated, yields pyromellitic anhydride and carbonised products.

The oxide [*mellitic anhydride*] (annexed formula) is obtained when mellitic acid is boiled under reflux with much benzoyl chloride during

six hours. It separates from boiling benzoyl chloride in colourless crystals, which are perfectly stable and non-hygroscopic. It is practically insoluble in cold water, but unites with warm water to form mellitic acid. It gives characteristic colorations with various solvents of high b. p.; thus with naphthalene, retene, phenanthrene, and fluorene it yields rose-red to bluish-red solutions, and with nitrobenzene a bluish-green solution. It darkens when heated above 320°. H. W.



Constituents of Essential Oils. [Degradation of the Diketone,  $C_{13}H_{20}O_2$ , Obtained from Selinene.] FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1913, **46**, 599—603. Compare this vol., i, 66, 188).—The diketone,  $C_{13}H_{20}O_2$ , obtained by the oxidation of natural selinene and also the diketo-monocarboxylic acid, obtained by the action of ozone on ortho(a)-elinene, have been further oxidised, whereby a tribasic acid,  $\begin{array}{c} CH_3-CH_2-CH-CH(CO_2H)-CH_2-CO_2H \\ | \\ CH_3-CH_2-CH-CO_2H \end{array}$ , has been obtained.

The diketone was most advantageously oxidised by a cold solution of bromine in aqueous sodium hydroxide. The acid,  $C_{13}H_{18}O_5$ , so obtained was purified by solution in alcohol and addition of chloroform, when the precipitated product was found to contain chloroform (about one mol. of chloroform to two mols. of acid), which could only be completely removed by heating it in a vacuum at the temperature of boiling xylene. The pure acid had m. p. 188°. Its tribasic nature was shown by converting it into the methyl ester,  $C_{13}H_{21}O_5$ , b. p. 200—205°,  $D^{20}_D$  1.140,  $n_D$  1.47948,  $a_D$  - 27°48', by the action of methyl iodide on the silver salt. The acid could be recovered unchanged after saponification of the ester.

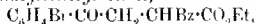
The same acid was obtained when the diketo-monocarboxylic acid,  $C_{13}H_{22}O_4$ , was oxidised by bromine in alkaline solution or by nitric acid.

II. W.

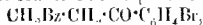
Studies in the cyclopentadiene Series. III. Certain Derivatives of 5-Nitro-2:3-dibenzoyl- $\Delta^{1:3}$ -cyclopentadiene. WILLIAM J. HALE and LAMBERT THORP (*J. Amer. Chem. Soc.*, 1913, **35**, 262—272. Compare A., 1912, i, 566; this vol., i, 184).—In the earlier papers, it has been shown that the formation of a cyclopentadiene ring by the condensation of a 1:3-dialdehyde with diphenacyl proceeds more slowly than with acetylacetone. A study has now been made of the behaviour of *pp'*-dimethyl-, *pp'*-dibromo-, and *p*-bromo-diphenacyl. The results show that the effect of methyl groups in the phenyl rings of diphenacyl is to retard the activity of the methylene groups of this ketone, whilst the presence of bromine atoms increases their activity.

By the condensation of *pp'*-dimethyldiphenacyl (Limpriht, A., 1900, i, 600) with sodium nitromalonaldehyde, 5-nitro-2:3-di-*p*-toluoyl- $\Delta^{1:3}$ -cyclopentadiene,  $NO_2-CH<\begin{array}{c} CH:C-CO-C_6H_4Me \\ CH:C-CO-C_6H_4Me \end{array}$ , was obtained in a yield of about 75% of the theoretical; it crystallises in yellow prisms, and decomposes at 243—244°. The silver salt decomposes at about 206°, and the monoxime at 150—151°.

Ethyl *p*-bromophenacylbenzoylacetate,

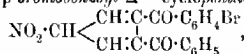


m. p. 81°; obtained in 75% of the calculated yield by the condensation of *p*-bromophenacyl bromide with the sodium derivative of ethyl benzoylacetate, forms colourless needles, and when boiled with dilute potassium hydroxide, is converted into *p*-bromodiphenacyl,



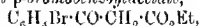


m. p. 116°, which crystallises in white plates with a pearly lustre. The yield of the latter compound amounted to 45% of the theoretical, 5-Nitro-3-benzoyl-2-*p*-bromobenzoyl- $\Delta^{1,2}$ -cyclopentadiene,

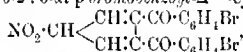


was obtained in a yield of about 75% of the calculated by the condensation of *p*-bromodiphenyl with nitromalonaldehyde; it forms small, yellow prisms and decomposes at 240—241°.

The sodium derivative of ethyl *p*-bromobenzoylacetate was prepared by Claisen's method. When the ester itself is warmed with aqueous ammonia, ethyl *p*-bromobenzoylacetate,

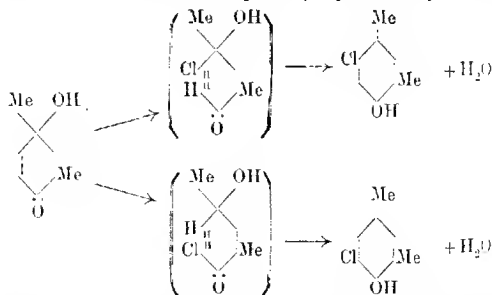


is obtained as a pale yellow, oily liquid which cannot be distilled without decomposition even under 5 mm. pressure. Its sodium derivative condenses with *p*-bromophenacyl bromide to form ethyl *p*-bromobenzoyl-*p*-bromophenacylacetate,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO} \cdot \text{C}_6\text{H}_4\text{Br}) \cdot \text{CO}_2\text{Et}$ , m. p. 75°, which crystallises in small, colourless prisms; a 60% yield of the theoretical was obtained. When this ester is boiled with dilute potassium hydroxide, it gives 30% of the calculated yield of *pp'*-dibromodiphenyl,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ , m. p. 182°, which forms lustrous, colourless plates, and condenses with nitromalonaldehyde with production of 5-nitro-2:3-di-*p*-bromobenzoyl- $\Delta^{1,2}$ -cyclopentadiene,



which forms yellow crystals and decomposes at 230—232°. E. G.

**Action of Hydrochloric and Hydrobromic Acids on 2:4-Dimethylquinol** [2:4-Dimethyl- $\Delta^{2,3}$ -cyclohexadiene-4-ol-1-one]. EUGEN BAMBERGER and EMIL REGER (*Ber.*, 1913, 46, 787—813).—It has been previously shown (Bamberger and Brady, A., 1901, i, 142) that aqueous sulphuric acid converts 2:4-dimethyl- $\Delta^{2,3}$ -cyclohexadiene-4-ol-1-one into *p*-xyloquinol. Hydrochloric acid, in aqueous solution, transforms it mainly into 5-chloro-*m*-4-xylenol and 6-chloro-*m*-4-xylenol, whilst, in anhydrous glacial acetic acid solution, the latter isomeride is alone obtained. The actions are probably represented by the scheme:



Under similar conditions, hydrobromic acid forms mainly 5-bromo-

*m*-4-xylenol and 6-bromo-*m*-4-xylenol. The identity of the products was also synthetically established. In the light of the present work, a modified interpretation is given to the observation of Bamberger, Bârdorf, and Szolayski (A., 1899, i, 311) that *p*-nitrosotoluene is converted by hydrochloric and hydrobromic acids into 3-chloro-*p*-cresol, in that hemiquinols are now assumed to be formed as intermediate products.

An improved method for the preparation of 1:3-dimethylphenylhydroxylamine is described (compare Bamberger and Brady, *loc. cit.*).

2:4-Dimethyl- $\Delta^{2:3}$ -cyclohexadiene-1-ol-1-one was heated during one hour at 100° with fuming hydrochloric acid, the mixture diluted with water, and extracted with ether. After drying the ethereal extract, the ether was removed, the residue was allowed to solidify as completely as possible, the solid portions filtered off, and the liquid part submitted to fractional distillation with steam. The following substances were obtained: 5-chloro-*m*-4-xylenol, b. p. 86.5–87°/9 mm. (*phenylurethane*, m. p. 129–130°; *p*-nitrobenzoate, white needles, m. p. 94–95°); 6-chloro-*m*-4-xylenol, white, silky needles, m. p. 90–91° (*benzoate*, glassy prisms, m. p. 84.5–85.5°); a substance, m. p. 169–170°, possibly chlorodixylenol; a substance, m. p. 190°, reddish-yellow needles, possibly chloro-*p*-xyloquinol; traces of *p*-xyloquinol and resin. In a second experiment, dixylenol was obtained in addition to *p*-xyloquinol and *p*-xyloquinone.

5-Chloro-*m*-4-xylenol was prepared by pouring a diazotised solution of 5-amino-*m*-4-xylenol into boiling cuprous chloride solution, and had b. p. 100–101°/17 mm. The phenylurethane and *p*-nitrobenzoate obtained from it were identical with those obtained above.

The synthesis of 6-chloro-*m*-4-xylenol was effected in the following manner: 6-nitro-*m*-4-xylidine was diazotised and treated with cuprous chloride solution, whereby 4-chloro-6-nitro-*m*-xylene, m. p. 12°, was obtained (compare Ahrens, *Annalen*, 1892, 271, 17). The latter was reduced by tin and hydrochloric acid to 6-chloro-*m*-4-xylidine, leaflets, m. p. 98.5–99°, which, according to Bamberger and Cadgène (*Dissert.*, 1903), is also formed by the action of concentrated hydrochloric acid on *as-m*-xylylhydroxylamine. The *hydrochloride*, *sulphate*, and *oxalate* were also prepared. The *acetyl* derivative forms silky needles, m. p. 158.5°. *Phenyl-1-chloro-m-xylylcarbamide*,  $C_6H_5Cl \cdot NH \cdot CO \cdot NHPh$ , white, silky needles, has m. p. 217–218° after previous softening. It immediately re-solidifies, melting again at 255° (decomp.). The corresponding *thiocarbamide* has m. p. 140–140.5° when rapidly heated. When slowly heated it melts at a lower temperature. Diazotisation and subsequent boiling of the aqueous solution converts 6-chloro-*m*-4-xylidine into 6-chloro-*m*-4-xylenol, which is identical with the substance described above.

The action of hydrogen chloride dissolved in glacial acetic acid on 2:4-dimethylcyclohexadienolone gave 6-chloro-*m*-4-xylenol, chloro-*p*-xyloquinol, traces of an oily chloroxylenol, resin, and, possibly, *p*-xyloquinol.

2:4-Dimethylcyclohexadienolone, when heated on the water-bath with aqueous hydrobromic acid, b. p. 122–123°, yielded 5-bromo-*m*-4-xylenol (which possibly contained small quantities of 6-bromo-*m*-4-

xylol, *as-m*-xylol, and *p*-xyloquinone), dixylenol, *p*-xyloquinol (or *p*-xyloquinone), and an amorphous acid.

To determine the constitution of the above bromoxylol, it was treated with bromine in glacial acetic acid solution. The product obtained, long, white needles, m. p. 179.5—180°, had the same m. p. as 2:3:6-tribromo-*p*-5-xylol (obtained by bromination of *p*-xylol) and 2:5:6-tribromo-*m*:4-xylol (obtained by brominating *m*-xylol), whilst mixtures of any of the three compounds showed no noticeable depression of m. p. When acted on by benzoyl chloride, however, the *benzoates*, m. p. 151—152°, obtained from 2:5:6-tribromo-*m*:4-xylol, and from the product of the successive action of hydrobromic acid and bromine on 2:4-dimethylcyclohexadienolone, proved to be identical, whereas 2:3:6-tribromo-*p*-xylol-5-benzoate had m. p. 128—129°; hence, the above monobromoxylol is probably 5-bromo-*m*:4-xylol. The *benzoate* and *phenylurethane* of the latter were prepared.

The direct synthesis of 5-bromo-*m*:4-xylol (compare Stoermer and Gühl, A., 1903, i, 848; Orton, Coates, and Burdett, T., 1907, 91, 53) was effected by the action of cuprous bromide solution on a diazotised solution of 5-amino-*m*:4-xylol hydrobromide. It had b. p. 121.5—122.5°/37 mm., and yielded a *benzoate*, m. p. 49—50.5°, and a *phenylurethane*, m. p. 136.5—137°, after previous softening, which proved to be identical with the above-mentioned products.

2:4-Dimethylcyclohexadienolone, when treated with hydrogen bromide in anhydrous glacial acetic acid solution, gave 6-bromo-*m*:4-xylol, m. p. 76—76.5°, 5-bromo-*m*:4-xylol, probably *p*-xyloquinone, possibly crude monobromo-*p*-xyloquinol and resin. The constitution of the solid bromoxylol follows from its identity with the product obtained from 6-nitro-*m*:4-xylidine by conversion of the latter into 4-bromo-6-nitro-*m*-xylene, reduction of this substance by iron filings and acetic acid to 6-bromo-*m*:1-xylidine and diazotisation of the latter substance (compare Noelting, Braun, and Thesmar, A., 1901, i, 589).

H. W.

**Preparation of Derivatives of *p*-Benzoquinone.** FAREWELL, VORM, MEISTER, LUCAS & BREXING (D.R.-P. 253391).—When the dinaphthylamino-*p*-benzoquinones (and their derivatives), obtained by the action of *p*-benzoquinone on  $\alpha$ - and  $\beta$ -naphthylamines, are heated with reagents having a high boiling point, they furnish highly coloured compounds, which after sulphonation are of technical importance.

Di-2-naphthylaminodichloro-*p*-benzoquinone,  $C_{20}O_2Cl_2(NH-C_{10}H_7)_2$  (obtained from tetrachloro-*p*-benzoquinone and  $\beta$ -naphthylamine, when boiled during three hours with nitrobenzene furnishes the compound,  $C_{22}H_{14}O_2NCl$ , glistening, green crystals, m. p. above 300°, whilst the isomeric compound from  $\alpha$ -naphthylamine has similar properties.

The compound,  $C_{22}H_{14}O_2N_2Cl$ , is obtained from di-2-naphthylaminodichloro-*p*-benzoquinone, whilst that from di-2-naphthylamino-*p*-benzoquinone,  $C_{20}H_{12}O_2(NH-C_{10}H_7)_2$ , forms a brownish-yellow powder.

F. M. G. M.

**Preparation of Chloroanthraquinones.** BADISCHE ANILIN- & SOODA-FABRIK (D.R.-P. 254450. Compare A., 1908, i, 991, and this vol., i, 49, 61).—The preparation of  $\alpha$ -chloroanthraquinones by the replacement of a nitro-group by chlorine has been described (*loc. cit.*), and the reaction has now been extended to the  $\beta$ -nitroanthraquinones.

When a suspension of 2-nitro-3-methylanthraquinone in trichlorobenzene is treated with chlorine at 150–180°, it gives rise to a yellow precipitate consisting of a mixture of  $\omega$ -2-tetrachloro- and  $\omega$ -2-trichloro-3-methylanthraquinones, which by the action of hot concentrated sulphuric acid, followed by treatment with sodium carbonate, furnishes a readily separable mixture of 2-chloroanthraquinone-3-carboxylic acid, m. p. 280°, and of 2-chloroanthraquinone-3-aldehyde, m. p. 229°, whilst the technical mixture of 1:6- and 1:7-dinitroanthraquinones give rise on similar treatment to 1:6-dichloroanthraquinone,  $C_{14}H_6O_2Cl_2$ , m. p. 202–204°. F. M. G. M.

**Preparation of 1-Halogen-2-aminoanthraquinones.** FARBWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253683. Compare A., 1904, i, 256).—When 2-aminoanthraquinone-3-sulphonic acid is treated with a halogen (1 mol.) it readily yields a 1-halogen-2-aminoanthraquinone-3-sulphonic acid, which by heating with 80% sulphuric acid is converted into the corresponding 1-halogen-2-aminoanthraquinone.

Sodium 1-chloro-2-aminoanthraquinone-3-sulphonate forms orange-red crystals; 1-chloro-2-aminoanthraquinone, yellow needles, m. p. 228–229°; sodium 1-bromo-2-aminoanthraquinone-3-sulphonate, orange-red leaflets, and 1-bromo-2-aminoanthraquinone, glistening, brownish-red leaflets, m. p. 305°, which on further bromination yields 1:3-dibromo-2-aminoanthraquinone. F. M. G. M.

**Preparation of Nitro-*p*-acyldiaminoanthraquinone.** FARBWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254185).—Nitro-*p*-acyldiaminoanthraquinones are readily obtained by the action of nitric acid (D 1.5) at temperatures not exceeding 25° on diacyl-1:4-diaminoanthraquinones, the nitro-group entering the ortho-position with respect to an amino-group.

2-Nitro-1:4-diacetyldiaminoanthraquinone forms yellowish-brown needles, m. p. 237° (decomp.), and on hydrolysis furnishes 2-nitro-1:4-diaminoanthraquinone as a blue, crystalline powder.

2-Nitro-1:4-diaminoanthraquinoneurethane, orange-red needles, m. p. 230–232°, is obtained in a similar manner from 1:4-diaminoanthraquinoneurethane. F. M. G. M.

**Preparation of Dianthraquinonylthio-ethers.** FARBENFABRIKEN vorm. FRIEDR. BAYER & CO. (D.R.-P. 254561).—Dianthraquinonyl thio-ethers are readily prepared by heating anthraquinone mercaptans.

$\beta\beta$ -Dianthraquinonyl thio-ether, yellow needles, is thus obtained from anthraquinone  $\beta$ -mercaptan; the isomeric  $\alpha\alpha$ -dianthraquinonyl thio-ether is a reddish-brown, crystalline powder, whilst  $\alpha\beta$ -dianthraquinonyl thio-ether is prepared by heating together molecular proportions of  $\alpha$ - and  $\beta$ -anthraquinone mercaptans.

6-Chloro-1-benzoylaminoanthraquinone when treated with sodium

sulphide furnishes 1-benzoylamincanthraquinone 6-mercaptan; this, when heated, gives rise to 1:1'-dibenzoyldiamino-6:6'-dianthraquinonyl thio-ether, which crystallises from nitrobenzene in yellow needles.

F. M. G. M.

**Anthraflavone-G.** EDUARD HEPP, RUDOLF UHLENHUTH, and FRITZ RÖMER (*Ber.*, 1913, **46**, 709—712).—To the above dye (D.R.-P. 190756) has been attributed the structure 1:2:5:6-diphthaloylanthracene (Bohn, A., 1910, i, 405). In its preparation by the action of calcium hydroxide on  $\omega$ -dichloromethylanthraquinone, the occurrence of large quantities of anthraquinone-2-carboxylic acid as by-product suggests that the first product of the reaction is anthraquinone-2-aldehyde, which then undergoes change into the corresponding acid and alcohol, the latter of which then condenses to anthraflavone. According to this view the dyo must be diphthaloylstilbene, and its formation by the action of lead oxide on 2-methylanthraquinone and its derivatives would be analogous to the well-known formation of stilbene from toluene. A convincing proof of the untenability of the older view with regard to the structure is given by the preparation of the dye in better yields than hitherto, from  $\omega$ -dibromo-2-methylanthraquinone by the action of copper powder or sodium iodide on solutions in nitrobenzene and acetone respectively.

The last method of preparation can be extended to substituted anthraflavones. 1-Chloro-2-methylanthraquinone, yellow needles, m. p. 171°, obtained from 2-methylanthraquinone-1-sulphonic acid by heating with potassium chlorate and hydrochloric acid, when treated with bromine in nitrobenzene solution is converted into 1-chloro- $\omega$ -dibromomethylanthraquinone, yellow leaflets, m. p. 176°; the action of sodium iodide on the acetone solution of this substance produces 1:1'-dichloro-anthraflavone (2:2'-dichloro-3:4:3':4'-diphthaloylstilbene), a yellow, crystalline powder.

The new formula for this class of dyo also gives a satisfactory explanation of other properties, such as the quantitative conversion into the corresponding anthraquinonecarboxylic acids. D. F. T.

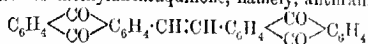
**2-Methylanthraquinone.** FRITZ ULLMANN AND KARL LUDWIG KLINGENBERG (*Ber.*, 1913, **46**, 712—725).—The authors have found that for the preparation of anthraquinone-2-aldehyde in larger quantities, the best method is by the intermediate formation of  $\omega$ -dibromomethylanthraquinone. The stilbene structure for anthraflavone (see Hepp, Uhlenhuth, and Römer, preceding abstract) is confirmed.

*Anthraquinone-2-aldehyde* can be obtained by the gradual addition of a mixture of chromic acid and acetic acid to a suspension of 2-methylanthraquinone in acetic anhydride containing a little sulphuric acid, and also by heating  $\omega$ -dibromomethylanthraquinone (prepared by the action of bromine on the methylanthraquinone in nitrobenzene solution at 150—160°) with concentrated sulphuric acid at 125—130°. The aldehyde forms pale yellow leaflets or needles, m. p. 188—189° (corr.). *phenylhydrazone*, reddish-violet needles, m. p. 242° (corr.); *oxime*, straw yellow needles, m. p. 238—239°; *semicarbazone*, yellow needles, m. p.

397° (corr.); *azine*, yellow needles, m. p. 410°: *sodium disulphite* compound, colourless crystals.

When a suspension of anthraquinone-2-aldehyde in dimethylaniline with zinc chloride is heated on a water-bath, condensation occurs; the same substance, 2-anthraquinonyltetramethyldiaminodiphenylmethane, is obtained when  $\omega$ -dibromomethylanthraquinone is warmed with dimethylaniline and zinc chloride; it crystallises in red needles, m. p. 240—241° (corr.), and can be oxidised to a green colouring matter.

The reaction between  $\omega$ -dibromomethylanthraquinone and dimethylamine or diethylamine follows a different course at the b. p. of the mixture, the product being the same as that from the action of copper powder on dibromomethylanthraquinone, namely, anthraflavone,

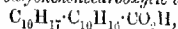


(diphthaloylstilbene, dianthraquinonylethylene), identical with the known dye; it is oxidised by sodium dichromate and nitric acid to anthraquinone-2-carboxylic acid, m. p. 283°, and when boiled with bromine in nitrobenzene solution yields the *dibromide*, m. p. above 400°; this on boiling with diethylaniline regenerates the anthraflavone.

If  $\omega$ -dibromomethylanthraquinone is heated at 240—250°, hydrogen bromide is eliminated and 2:2'-dianthraquinonylacetylene *dibromide*, yellow needles, m. p. 360°, is obtained; when heated with diethylaniline or alkali phenoxide, the last substance is converted into 2:2'-dianthraquinonylacetylene (*diphthaloylstilbene*), yellow leaflets, m. p. 350—353°, which unites with bromine to yield the dibromide, and is oxidised by chromic acid in the presence of nitric acid to anthraquinone-2-carboxylic acid; it can also be reduced by hyposulphite to a red vat, which dyes cotton yellow.

D. F. T.

**Action of Carbon Dioxide on the Magnesium Compound of Fenchyl Chloride.** GUSTAV KOPPE and S. V. HINTIKKA (*Ber.*, 1913, 46, 645—648).—Fenchyl chloride reacts with magnesium in the course of a week, and when carbon dioxide is passed through the product, the reaction leads to as complicated a mixture as Houben experienced in the case of pinene hydrochloride (*A.*, 1893, i, 42). When the ethereal extract is shaken with sodium carbonate it gives, starting from inactive fenchyl chloride, a clear aqueous solution containing hydrofenchene-carboxylic acid and an emulsion from which a small quantity of *hydrodifenchene-carboxylic acid*,



may be isolated in the form of long, glistening needles, m. p. 106°, whilst the predominating, neutral portion, on fractionation, yields an almost inactive *hydrodifenchene*,  $\text{C}_{20}\text{H}_{34}$ , as a glycerol-like liquid, b. p. 135—137°/10 mm.,  $D_4^{20}$  0.9564,  $n_D^{20}$  1.50928, and also inactive fenchene, and probably some fenchyl alcohol.

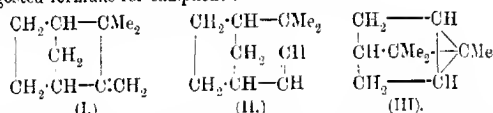
Active fenchyl chloride,  $\alpha_D^{25} - 6.6^\circ$ , however, gives a better yield of *hydrofenchene-carboxylic acid*,  $\text{C}_{10}\text{H}_{17} \cdot \text{CO}_2\text{H}$ , in the form of a white, very soluble, inactive mass, b. p. 140—142°/20 mm., m. p. 52—53°, which yields an *amide*, m. p. 107°, and an *anilide*, m. p. 105—106°. On the other hand, no *hydrodifenchene-carboxylic acid* is obtained, and less neutral substances are formed, from which active *hydrodifenchene*,

b. p. 155—156°/10 mm.,  $D_4^{20}$  0.9652,  $n_D^{20}$  1.51299,  $\alpha_D^{18} + 5.30'$ , and an active fonchone,  $\alpha_D^{20} + 4.17'$ , have been isolated. J. C. W.

**Preparation of Esters of Dibromo- $\beta$ -phenylpropionic Acid.** FARNENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254666. Compare this vol. i, 63).—*Fenchyl dibromo- $\beta$ -phenylpropionate*, colourless, tasteless prisms, m. p. 105°, and of therapeutic value, is readily prepared by heating together fenchyl alcohol and dibromo- $\beta$ -phenylpropionyl chloride in benzene solution. F. M. G. M.

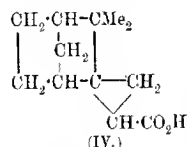
**Preparation of a Fenchyl Ester.** CHEMISCHE FABRIK VON KERESZTY, WOLF & Cie (D.R.-P. 253756).—*Fenchyl salicylate*, m. p. 51°, is of therapeutic value, and can be prepared by known methods from fenchyl alcohol and salicylic acid (or methyl salicylate). F. M. G. M.

**The Constitution of Camphene.** EDUARD BUCHNER and WILHELM WEIGAND (*Ber.*, 1913, 46, 759—768).—Of the three suggested formulæ for camphene:



the first (Wagner's formula) has been received with most favour (compare Semmler, A., 1909, i, 170; Harries and Palmén, A., 1910, i, 497; Komppa, A., 1911, i, 388), and has received additional support from molecular refractivity considerations (von Auwers, A., 1912, ii, 214). A final decision on purely chemical grounds appears to be possible by the application of ethyl diazoacetate.

It has already been shown that benzene and ethyl diazoacetate couple with loss of nitrogen to form ethyl norcaradienecarboxylate,  $\text{CH:CH:CH} \rightarrow \text{CH:CO}_2\text{H}$ , which after hydrolysis can be oxidised to cyclopropane-*trans*-1:2:3-tricarboxylic acid (Braren and Buchner, A., 1901, i, 385). If this reaction could be applied generally, a substance



of formula I should yield 2:2-dimethylnorcamphane-3-*spiro*cyclopropanecarboxylic acid (formula IV annexed), which might be oxidised to cyclopropane-1:1:2-tricarboxylic acid; a substance of formula II would give finally cyclopropane-1:2:3-tricarboxylic acid, whilst a substance of formula III would not react with ethyl diazoacetate. Experiment gives results in entire accord with the first of these

possibilities, thus providing apparently final evidence in favour of formula I.

It is interesting to note that the condensation product of ethyl diazoacetate and camphene is a *spirane* molecule with three-ring systems, this view being supported by determinations of the molecular refraction and dispersion.

The camphene used was mainly prepared from bornyl chloride by the action of aniline (Ullmann and Schmid, A., 1911, i, 70); the same condensation product was always obtained. For the condensation, a mixture of 5 grams of camphene with 5 grams of methyl diazoacetate was gradually added to 30 grams of camphene (m. p. 44–45°; b. p. 156–157°/745 mm.;  $[\alpha]_D^{20} + 62.59^\circ$ ) containing 1 gram of copper powder as catalyst, at 160–165°. A practically theoretical volume of nitrogen is liberated, and methyl 2:2-dimethylnorcamphane-3-spirocyclopropanecarboxylate is obtained as a colourless oil, b. p. 126°/14 mm.,  $[\alpha]_D^{20} + 6.73^\circ$ ,  $D_4^{20} 1.0268$ ,  $n_D^{20} 1.48567$ , with an odour resembling camphene; in suspension in sodium carbonate solution it is stable towards potassium permanganate. The corresponding ethyl ester, obtained by the application of ethyl diazoacetate, has b. p. 128–136°/14 mm. The esters can be hydrolysed to the corresponding acid (formula IV) by alcoholic potassium hydroxide, and the product was purified by conversion into the acid chloride, which is changed by concentrated aqueous ammonia into the amide, colourless leaflets, m. p. 124°; 2:2-dimethylnorcamphane-3-spirocyclopropanecarboxylic acid, obtained by hydrolysis of this, forms colourless needles, m. p. 108°; the calcium, barium, lead, and silver salts were obtained by precipitation from an aqueous solution of the ammonium salt. When an intimate mixture of the amide with sodium hypobromite solution is warmed on a water-bath, 2:2-dimethylnorcamphane-3-spiroaminocyclopropane is produced as an unpleasant smelling oil; hydrochloride, colourless leaflets, m. p. 253° (decomp.); yellow aurichloride, m. p. 160° (decomp.); platinichloride, golden prisms decomposing at 237°; yellow picrate, m. p. 201°.

If the methyl ester obtained by the condensation of camphene and methyl diazoacetate is treated in alcoholic solution with sodium, it becomes reduced to 2:2-dimethylnorcamphane-3-spirocyclopropanemethylol,  $C_{11}H_{17} \cdot CH_2 \cdot OH$ , a colourless, viscous liquid, b. p. 129°/12 mm.,  $[\alpha]_D^{20} + 26.79^\circ$ ,  $D_4^{20} 0.9972$ ,  $n_D^{20} 1.50205$ , with an odour resembling that of camphene; phenylurethane, needles, m. p. 234°.

The oxidation of 2:2-dimethylnorcamphane-3-spirocyclopropanecarboxylic acid was effected in dilute sulphuric acid by potassium permanganate, the last substance is added as required, and the process occupies many hours; the oxidation tends to proceed too far, and only a relatively small quantity of cyclopropane-1:1:2-tricarboxylic acid was obtained, which on heating lost carbon dioxide with formation of a mixture of cyclopropane-1:2-cisdicarboxylic acid and the corresponding anhydride; acetyl chloride dehydrated this to the pure anhydride, which was definitely recognisable.

D. F. T.

**The Constituents of Ethereal Oils.** High boiling Camphor Oil. FRIEDRICH W. SEMMLER and IRENE ROSENBERG (*Ber.*, 1913, 46, 768–774).—A more careful investigation of the constituents of the blue-coloured, high-boiling camphor oil (compare Schimmel & Co., A., 1909, i, 816).

The oil was separated by distillation into three fractions, b. p. 130–150°/10 mm., 150–170°/10 mm., and 170–190°/10 mm.

The first fraction contained limene and a little cadinene, which were

VOL. CIV. L.

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identified by their hydrogen chloride additive compounds; limene trihydrochloride, m. p. 79°, has before solidification the following properties, b. p. 177—189°/8 mm.,  $D^{20}_D$  1.0370,  $n_D$  1.50152,  $[\alpha]_D \pm 0^\circ$ . The presence of three ethylenic linkings in limene was proved by reduction in acetic acid with hydrogen and platinum black to *hexahydrolimene*, an optically inactive liquid, b. p. 123—125°,  $D^{20}_D$  0.8244,  $n_D$  1.45423. This fraction also contained a sesquiterpene,  $C_{15}H_{24}$ , b. p. 129—133°,  $D^{20}_D$  0.9015,  $n_D$  1.50058,  $[\alpha]_D + 3^\circ$ , for which the name *sesquicamphene* is suggested; although the data suggest a bicyclic diolefinic substance, no solid hydrogen chloride additive compound was obtainable.

The second fraction had as almost sole constituent a sesquiterpene alcohol,  $C_{15}H_{26}O$ , b. p. 159—162°,  $D$  0.95413, for which the name *sesquicamphenol* is suggested; it was purified by conversion into the sodium alcoholate and regeneration by treatment with water; by heating with potassium hydrogen sulphate at 180° for two hours a molecule of water is eliminated with formation of a hydrocarbon, b. p. 125—130°,  $D^{20}_D$  0.9138,  $n_D$  1.50895,  $[\alpha]_D + 50^\circ$ , which is probably a reduced naphthalene derivative; no solid hydrochloride was obtainable.

The least volatile fraction consisted chiefly of hydrocarbons, from which small quantities of oxygen compounds were removed by heating with sodium; the purified product, b. p. 180—190°/11 mm.,  $D^{20}_D$  0.9276,  $n_D$  1.51986,  $[\alpha]_D + 1^\circ$ , is a diterpene,  $C_{20}H_{32}$ , a class of substance generally absent from ethereal oils. If this crude product is treated in ethereal solution with hydrogen chloride, a *tetrahydrochloride*, thin tablets, m. p. 129—131°, is obtained, from which the hydrocarbon can be regenerated in a purer condition by treating successively with a mixture of sodium acetate and acetic acid and then alcoholic potassium hydroxide; it then has b. p. 177—178°/6 mm.,  $D^{20}_D$  0.8870,  $n_D$  1.50339,  $[\alpha]_D \pm 0^\circ$ . This monocyclic hydrocarbon, for which the name  *$\alpha$ -camphorene* is proposed, is reduced by hydrogen and platinum black to *octahydro- $\alpha$ -camphorene*,  $C_{20}H_{34}$ , b. p. 174—176°/9 mm.,  $D^{20}_D$  0.8526,  $n_D$  1.46470,  $[\alpha]_D \pm 0^\circ$ . From the oily residue obtained in the preparation of the tetrahydrochloride, could be regenerated by alcoholic potassium hydroxide a bicyclic isomeride,  *$\beta$ -camphorene*,  $C_{20}H_{32}$ , b. p. 170—180°/10 mm.,  $D^{20}_D$  0.930,  $n_D$  1.518°,  $[\alpha]_D \pm 0^\circ$ , which gives no solid additive compound with hydrogen chloride.

The blue colour of all high-boiling fractions of camphor oils is due to such small traces of a coloured substance that no particulars of its composition could be determined.

D. F. T.

**Caoutchouc and Guttapercha Resins.** G. H. HILLEN (*Arch. Pharm.*, 1913, 251, 94—121).—Proximate analyses have been made of the resinous portions of various kinds of caoutchouc and allied products.

The resinous portion of "pontianac," "bresk" or "dead Borneo," an inferior "rubber" obtained from the latex of *Dyera costulata*, Hook, was found to contain lupeol acetate,  $\alpha$ -amyrin acetate,  $\beta$ -amyrin acetate, and a resin (compare Sack and Tollens, A., 1904, i, 1011; Cohen, A., 1907, i, 211, 230). The formula  $C_{30}H_{48}O$  is suggested for lupeol.

The caoutchouc (Ceara rubber) of *Manihot glaziovii*, prepared by the

lewa process in German East Africa, contains 7% of resin, composed of isopholesterol acetate, a soft resin, and a green, amorphous substance.

Guayule caoutchouc contains 16% of resin, composed of soft resinous material, probably formed by the oxidation of the essential oil contained in the plant, which contains no substances giving the phytosterol reactions (compare Alexander, A., 1911, i, 897).

"Malabuwai guttapercha" from *Alstonia grandifolia*, Miq., contains  $\alpha$ -amyirin acetate,  $\beta$ -amyirin acetate, an oily substance, and traces of a yellow resin.

The resin of *Palaequium Gutta* from German New Guinea contains lupcol, cinnamate, an oily substance, and a small quantity of a resin.

A table giving the percentages of resin, the appearance of the resins under the microscope, and their reactions with the usual phytosterol reagents for a number of commercial caoutchoucs is provided.

The colour reactions of most of the substances referred to in the paper with phytosterol reagents are tabulated. T. A. H.

**The Viscous Transformation of Caoutchouc.** A. von ROSSEM (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 78—83).—According to Gorter (*Mededelingen over Rubber*, 1911) the transformation of ordinary caoutchouc into the viscous, glue-like modification under the influence of heat, light, and certain chemical reagents is due to depolymerisation. It is suggested that normal polymerised caoutchouc is under ordinary conditions metastable, and that the formation of the viscous variety simply corresponds with the transition from the metastable to the stable form. In support of this view, Gorter describes experiments which show that if a benzene solution of caoutchouc, prepared and kept in the dark, is mixed with a caoutchouc solution which has been exposed to sunlight for some time, the viscosity of the mixed solution gradually diminishes when the solution is protected from the light by means of red glass. In exactly similar circumstances, the viscosity of the original solution was found to remain constant, and the difference in behaviour is supposed to be due to the "inoculation" of the original solution with the stable modification when this solution is mixed with the insolated solution.

To test this theory, measurements of the viscosity of 1% solutions of caoutchouc have been made, with special reference to the influence of light. After exposure to the light from an arc lamp for some hours, the viscosity is found to have diminished, but the subsequent fall is very slow if the solution is kept in the dark, and does not differ from that exhibited by a portion of the original solution which has not been exposed to the arc light. If diffused daylight is allowed access to the solution, the subsequent fall in the viscosity is very much more rapid.

Similar experiments were made with solutions exposed to the light from a Uviol lamp. The results obtained in both series show that there is no after-effect of the light in so far as the viscosity of the solutions is concerned. In some of these experiments the caoutchouc solutions were exposed to the Uviol lamp in glass vessels, whilst in others, quartz vessels were employed. After six and three-quarter

hours' exposure, the time of out-flow of a certain volume of solution was found in a particular case to have fallen from 560 to 412 seconds with the glass apparatus, whilst the time required by the solution after exposure in the quartz tube was only 56 seconds. These results indicate that the active rays are the short-waved rays which are absorbed by glass.

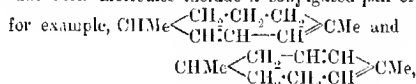
H. M. D.

The Hydrohaloids of Artificial and Natural Caoutchoucs, and the Caoutchouc-like Substances Regenerated from Them. CARL D. HARRIES (*Ber.*, 1913, 46, 733-743).—Contrary to the statement of Weher (*A.*, 1900, i, 353), caoutchouc forms additive compounds with hydrogen bromide and hydrogen iodide, as well as with hydrogen chloride. The method followed was to saturate the chloroform solution of the caoutchouc with the gas, and then after several hours to precipitate by alcohol.

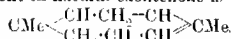
Natural caoutchouc unites with two molecules of each acid, forming substances:  $C_{10}H_{18}Cl_2$ ,  $C_{10}H_{18}Br_2$ ,  $C_{10}H_{18}I_2$ ; guttapercha, caoutchouc obtained by the polymerisation of isoprene under the influence of heat and of sodium, and also caoutchouc obtained from dimethylbutadiene, behave in a similar manner, except that the additive compounds of the two former synthetic caoutchoucs with hydrogen iodide, after precipitation, contain only one molecule of hydrogen iodide.

The halogen hydride is only partly removed by treatment with organic bases, but pyridine and piperidine at 125–145° act on the compounds, if necessary in benzene solution, with elimination of the two molecules of hydric acid. The products are not identical with natural caoutchouc, but resemble more the synthetic substance obtained by the action of sodium (Harries, *A.*, 1911, i, 798). The elimination of halogen hydride by heating with sodium hydroxide or sodium amide gives a halogen-free caoutchouc, which, however, is apparently different from the natural product and from that obtained by polymerisation with sodium. The dihydrochloride of guttapercha, when treated for the elimination of two molecules of hydric acid, yields a compound resembling caoutchouc, possibly indicating a conversion of guttapercha into caoutchouc.

From a consideration of the difficulty with which the above new forms of caoutchouc undergo ozonisation, it is tentatively suggested that their molecules include a conjugated pair of ethylenic linkings.



whilst the arrangement in natural caoutchouc is



[With EWALD FOXROBERT.]—From natural caoutchouc were prepared the dihydrochloride, *dihydrobromide*, and *dihydr iodide*; from caoutchouc obtained by polymerisation on warming, were prepared a *dihydrochloride*, *dihydrobromide*, and a *hydr iodide*; "sodium polymerised" caoutchouc yielded a *dihydrochloride*, a *hydrobromide*, and a *hydr iodide*; "dimethylbutadiene" caoutchouc yielded a *dihydrochloride*, *dihydro*

bromide, and a *dihydriolide*; guttapercha yielded a *dihydrochloride*, *dihydrobromide*, and a *dihydriolide*. Although affected by hydrofluoric acid no hydrofluoride was obtainable from any of the preceding hydrocarbon substances. The above hydrohaloids are amorphous, sometimes viscous, substances, which undergo decomposition at temperatures between 100° and 200°.

The caoutchouc regenerated from the dihydrochlorides by treatment with pyridine or piperidine at 125–135° resembles "sodium isoprene" caoutchouc in solubility and slow absorption of ozone to produce a diozonide, but yields a relatively stable *dihydrobromide* and *dihydriolide*.

D. F. T.

Theory of Vulcanisation. DAVID SPENCE (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 84–85).—Polomical against Kindscher and Hinrichsen (A., 1912, i, 1007) and Ostwald (A., 1912, i, 706).

H. M. D.

$\alpha$ - and  $\beta$ -Antiarin and on Crystallised Albumin from Antiaris Latex. HEINRICH KULANI (*Ber.*, 1913, 46, 667–680). Compare A., 1897, i, 91, and A., 1911, i, 138).—Crystallised rhamnose, m. p. 93–94°, and antiarigenin, m. p. 188°, have been obtained from  $\beta$ -antiarin by means of dilute hydrochloric acid. The  $\alpha$ - and  $\beta$ -antiarins only differ in their sugars, and careful analyses lead to the formulae  $C_{27}H_{36}O_{10} \cdot 4H_2O$  and  $C_{27}H_{36}O_{10} \cdot 3H_2O$  respectively, whilst antiarigenin receives the formula  $C_{21}H_{28}O_9$ . The hydrolysis of these glucosides by means of dilute acids is accompanied by the extensive formation of resinous matter, which seems to indicate the presence of a labile aldehyde or ketone group in antiarigenin. The action of the common moulds is quite unavailing, although the glucosides soon disappear from unpreserved antiaris latex, which may, therefore, contain a specific enzyme.

Antiarase could not be obtained crystalline, but the lactone of antiaronic acid, well-defined monoclinic crystals of the epidote type, has been converted into the following derivatives, which differ from those of the known metameric acids: *phenylhydrazone*, long needles, m. p. 143–145°; *quinine* salt, very slender needles, m. p. 180–181°, more soluble in cold water than the *quinine* salt of rhammonic acid, which forms nodules of silky needles, m. p. 180–182°; *brucine* salt, small, pointed needles with  $2H_2O$ , m. p. 118–119°; *brucine* salt of rhammonic acid, large crystals with  $7H_2O$ , m. p. 120–126°.

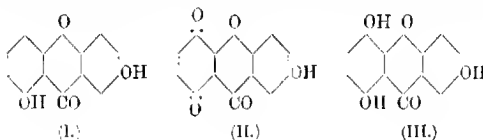
$\alpha$ -Antiarin is considerably attacked by sodium amalgam, and forms an *azine*,  $C_{27}H_{31}O_{10}N_2 \cdot 2H_2O$ , m. p. 236–240°, which, however, like the parent substance, is unaffected by aluminium amalgam in the cold. Antiarigenin yields a *semicarbazone*,  $C_{21}H_{21}O_9N_3$ , which begins to sinter at 225°.

Attempts to oxidise the glucosides with silver oxide or hydrogen peroxide were without result, but the action of chromic acid, nitric acid, or permanganate promises to throw light on their constitution.

"Antiaris residue," the portion of the latex which is insoluble in alcohol, contains a protein which may be extracted to the extent of 6.5%, by means of 0.8% acetic acid (compare Kotake and Knoop,

A., 1912, ii, 81). It may be recrystallised from hot 10% acetic acid in the form of white, hygroscopic crystals, which darken at 250°,  $[\alpha]_D -15.2^\circ$ . The substance may be titrated, using phenolphthalein, but it could not be shown that the magnesium which accompanies the crude protein is combined as a salt. J. C. W.

**Anthocyanin. III. An Anthocyanin-like Oxidation Product of Euxanthone.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1913, 46, 649—650. Compare A., 1912, i, 42, 292).—When euxanthone (2:8-hydroxyxanthone) (I), which is obtained by treating Indium yellow with hydrochloric acid and ammonia, is oxidised by chromic acid in glacial acetic acid, 2-hydroxy-5:8-quinoxanthone (II) is formed in small, sparkling, deep red needles, which give a blue solution in alkalis and a red in concentrated sulphuric acid. On reduction with zinc dust in acetic anhydride suspension, an amorphous product is obtained, which, on hydrolysis, yields 2:5:8-trihydroxyxanthone (III) in small, light yellow, silky needles with  $2H_2O$ , m. p. 328—330°. This compound, like its isomeride, gentisein, gives a blood-red colour with sodium amalgam, and its alcoholic solution dyes mordanted cotton. It forms a triacetyl derivative,  $C_{19}H_{14}O_5$ , in faintly yellow needles, m. p. 236—230°, and with diazomethane a trimethoxyxanthone,  $C_{16}H_{14}O_5$ , in pale yellow needles, m. p. 194—195°.



J. C. W.

**Action of Sodium Methoxide on Bilirubin Acid, Bilirubin, and Hemibilirubin.** MAX FISCHER and HEINRICH RÖSE (*Ber.*, 1913, 46, 439—442).—Bilirubin and hemibilirubin resemble the earlier examined pyrrole derivatives (this vol., i, 71, Fischer and Bartholomäus, this vol., i, 209) in their behaviour towards sodium methoxide at elevated temperatures. When heated with sodium methoxide in alcoholic solution at 220—230°, each gives rise to 2:4:5-trimethylpyrrole-3-propionic acid (identified by the picrate; compare Fischer and Bartholomäus, *loc. cit.*), together with a little xanthobilirubic acid (see below).

Bilirubic acid under similar treatment gives in good yield an acid substance, yellow prisms, m. p. 274°, for which the name *xanthobilirubic acid* (or *xanthopyrrolecarboxylic acid*) is proposed; sodium salt sparingly soluble. It is possible that the acid is the pure form of the dehydrilic acid of Piloty and Thannhauser (A., 1912, i, 925). On reduction by a mixture of hydriodic and acetic acids it is reconverted into bilirubic acid.

The above results must be regarded as a proof of the presence of a third pyrrole ring in bilirubin and hemibilirubin. D. F. T.

**The Identity of Baphinitone with Homopteroearpin.** HUGH RYAN and R. FITZGERALD (*Proc. Roy. Irish Acad.*, 1913, 30, 106—108).—Baphinitone,  $C_{27}H_{46}O_4$ , obtained from barwood, forms colourless, acicular crystals, m. p.  $84^\circ$  (Anderson, T., 1876, ii, 582, gives m. p. about  $88^\circ$ , and formula  $C_{26}H_{46}O_4$ ). In 4% solution in chloroform it has  $[\alpha]_D^{20} - 211.7^\circ$ . Similarly, homopteroearpin, obtained from santalin by the method of Cazeneuve and Hugoueney (A., 1887, 971; 1889, 169), was found to melt at  $84^\circ$  (Brooks, A., 1911, i, 154, gives  $86^\circ$ ), and to have  $[\alpha]_D^{20} - 211^\circ$  in 4% solution in chloroform. In appearance, solubility and m. p., homopteroearpin is identical with baphinitone, and a mixture of the two substances melts at the same temperature as each of its constituents.

A solution of homopteroearpin in chloroform reacts readily with bromine in bright sunlight with the formation of a substance,  $C_{27}H_{41}Br_2O_4$ , colourless needles, m. p.  $200^\circ$ , and of a yellow, amorphous solid. Contrary to Cazeneuve's statement, homopteroearpin does not yield methyl iodide when treated with hydriodic acid, and thus contains no methoxy-group; nevertheless, a phenolic substance is obtained by the action of hydriodic acid on it.

H. W.

**Optical Activity of Tannin.** EMANUEL NAVASSART (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 97—99).—The rotatory power of tannin solutions has been examined with reference to the influence of concentration. In the case of aqueous solutions, the rotatory power varies very considerably with the concentration, the value of  $[\alpha]_D^{20}$  increasing from  $49.8^\circ$  to  $89.7^\circ$  when the concentration falls from 20% to 0.08%. When dissolved in ethyl alcohol, acetone, and acetic acid, the rotatory power of tannin is much smaller, and varies less with the concentration. For concentrations between 1% and 20%, the observed values of  $[\alpha]_D^{20}$  vary from  $12.7^\circ$  to  $16.9^\circ$  in alcohol, from  $12.9^\circ$  to  $15.1^\circ$  in acetone, and from  $9.4^\circ$  to  $14.5^\circ$  in acetic acid. These results seem to show that the rotatory power of the tannin increases as the degree of dispersity of the substance in the various solvents diminishes.

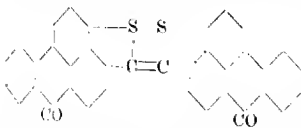
H. M. D.

**[Preparation of Derivatives of Benzanthrone Containing Sulphur.]** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE (D.R.-P. 254038).

—The action of chlorine (or chlorinating reagents) on 2-methylbenzanthrone (m. p.  $199^\circ$ ) gives rise to chloromethylbenzanthrone, m. p.  $175^\circ$ ; this, when heated with sulphur or polysulphides during two hours at  $200-240^\circ$ , yields the compound (annexed formula), glistening, coppery needles.

The preparation of bromomethylbenzanthrone, dichloro-2-methylbenzanthrone, and of nitro- and amino-benzanthrone with their sulphur derivatives is also described.

F. M. G. M.



Preparation of Homologues of Hydroquinine. VEREINIGTE CHUNINFABRIKEN ZIMMER & Co. (D.R.P. 254712. Compare A., 1892, 1253).—The alkylation of hydrocupreine has furnished the following derivatives: *Ethylhydrocupreine*,  $C_{21}H_{25}O_2N_2$ , is amorphous, but its *sulphate* forms colourless needles, whilst *propylhydrocupreine*,  $C_{22}H_{30}O_2N_2$ , colourless crystals, has m. p. 143°. F. M. G. M.

Alkaloids of Javanese Coca [*Erythroxyton novogranatense*]. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1911, 30, 204–210; 1912, 31, 249–259. Compare A., 1906, ii, 315).—The method of analysis previously described has been slightly modified, since it is found that the insoluble barium salts, obtained by heating the alkaloids with barium hydroxide, contain small quantities of barium cinnamate in addition to barium  $\beta$ -truxillate. The cinnamic acid is recovered by agitating the mixed acids with chloroform. The mixed acids obtained from the soluble barium salts are also treated with chloroform, when  $\alpha$ -truxillic acid, possibly containing also the  $\beta$ -isomeride, remains. The acids obtained from the chloroform solution were found to contain about 50·3% cinnamic acid and 37·9% benzoic acid.

A second specimen of mixed acids was obtained by decomposing the alkaloids by means of hot hydrochloric acid and solution of the product in ether, which left a small residue of impurities. The ethereal solution was shaken with potassium hydroxide, the latter acidified with hydrochloric acid, and again treated with ether, whereby a small quantity of  $\alpha$ -truxillic acid remained undissolved. The ethereal solution was evaporated to dryness, and the residue extracted with chloroform, which left a small residue consisting of a mixture of  $\alpha$ - and  $\beta$ -truxillic acids. The acids obtained from the chloroform solution contained 52·1% cinnamic acid, and 34% benzoic acid mixed with acids of higher molecular weight or with neutral substances.

In the second paper the author has worked out a process for the separation of the acids obtained by the decomposition of the alkaloids of Javanese coca, and has ascertained the presence of the following substances in a specimen of these acids: cinnamic, benzoic, *allo*-cinnamic,  $\alpha$ -truxillic,  $\beta$ -truxillic and  $\delta$ -truxillic acids, resinous acids, and neutral substances, together with an acid, m. p. about 156° (probably identical with protococic acid obtained by Hesse, A., 1903, i, 192), and an acid, m. p. about 190°, possibly identical with  $\beta$ -cocic acid.

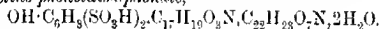
The properties of the truxillic acids and their salts have been investigated. The former are insoluble in light petroleum, but are dissolved in the presence of benzoic or cinnamic acids, the solubility of the  $\alpha$ - and  $\gamma$ -acids being, however, only slightly affected.  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Truxillic acids are only sparingly soluble in chloroform at the ordinary temperature. Hot chloroform dissolves the  $\beta$ -acid, particularly in the presence of benzoic and cinnamic acids. The  $\delta$ -acid is soluble in chloroform. The  $\alpha$ - and  $\gamma$ -acids are insoluble in benzene, whereas the  $\beta$ - and  $\delta$ -acids are more soluble in the hot than in the cold solvent. The latter acids may be crystallised from boiling water, in which the  $\alpha$ - and  $\gamma$ -acids are but slightly soluble.

One hundred c.c. of an aqueous solution of barium  $\beta$ -truxillate, saturated at  $26^{\circ}$ , contain 0.028 gram of the salt.

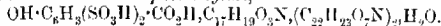
The following salts are sparingly soluble in water: the zinc, cadmium, iron, lead, copper, mercury, and silver salts of the  $\alpha$ -acid; the calcium, barium, strontium, zinc, cadmium, manganese, iron, cobalt, nickel, lead, copper, mercury, and silver salts of the  $\beta$ -acid; the lead, copper, mercury, and silver salts of the  $\gamma$ -acid; the same salts of the  $\delta$ -as of the  $\beta$ -acid, and in addition the magnesium salt. The magnesium salt of the  $\beta$ -acid is soluble in water.

H. W.

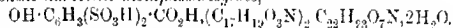
**Preparation of Therapeutically Valuable Double Salts from Morphine and Narcotine.** C. F. BOEHRINGER & SOHNEN (D.R.P. 234502).—The following therapeutically valuable double salts are readily obtained by treating a hot alcoholic solution of the acid with the requisite amount of the other components. *Morphine narcotine meconate*,  $C_7H_4O_7 \cdot C_{17}H_{19}O_5N \cdot C_{22}H_{23}O_7N \cdot 4H_2O$ . *Morphine dinarcotine benzenetrisulphonate*,  $C_6H_5(SO_3H)_3 \cdot C_{17}H_{19}O_5N \cdot (C_{22}H_{23}O_7N)_2 \cdot 2H_2O$ . *Morphine narcotine phenoldisulphonate*,



*Morphine dinarcotine disulphosacetylate*,



*Dinarcotine narcotine disulphosacetylate*,



*Morphine narcotine sulphate*,  $H_2SO_4 \cdot C_{17}H_{19}O_5N \cdot (C_{22}H_{23}O_7N)_2 \cdot H_2O$ . They form colourless crystals, sparingly soluble in cold, readily in hot water, and somewhat insoluble in the ordinary organic media.

F. M. G. M.

**Preparation of Morphine Esters of Alkyl- and Aryloxy-fatty Acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.P. 254094).—*Diethoxycetylmorphine*, an oil, is prepared by heating morphine (10 parts) with ethoxycetic anhydride (37 parts) during several hours at  $40$ – $45^{\circ}$ ; the *hydrochloride*, glistening leaflets, decomposes at about  $142^{\circ}$ .

*Ethoxycetylmorphine*, m. p.  $155^{\circ}$  (about), is obtained accompanied by the foregoing compound when the proportions of the reacting components are varied, and the mixture heated at  $40$ – $50^{\circ}$ ; the *hydrochloride*, needles, has m. p.  $183$ – $186^{\circ}$ . *Diphenoxycetylmorphine*, m. p.  $125^{\circ}$  (decomp.), faintly-coloured crystals, is prepared in an analogous manner.

F. M. G. M.

**Alkaloids of Pareira Root.** MAX SCHOLTZ (Arch. Pharm., 1913, 251, 136–151. Compare A., 1913, i, 87, and Faltis, 1912, i, 796).—As the result of further analyses, the author now reverts to the formula  $C_{25}H_{35}O_5N$ , which he used originally for the bebeerines. Bebeerine, isobeeberine, and  $\beta$ -bebeerine can all be represented by the extended formula  $OH \cdot C_{15}H_{21}O_4(OMe) \cdot NMe$ . The first and third isomerides yield with acetic anhydride the same optically inactive hydroxytriacetylbebeerine. The latter appears to be formed by the opening of a ring containing nitrogen, the attachment of an acetyl group to the N-atom, and of the residue  $CH_2 \cdot CO \cdot O$  to the carbon atom formerly linked to the N-atom.



isoBebeerine yields two hydroxytriacetylisobebeerines, one dextro-rotatory and the other inactive.

isoBebeerine,  $C_{18}H_{21}O_3N$ , m. p.  $297^\circ$  (decomp.), is the chief constituent of "crystallised bebeerine sulphate" (Merck); the *hydriodide*, m. p.  $300^\circ$  (approx. decomp.), forms prisms from water; the *hydrochloride* is precipitated as colourless needles on adding hydrochloric acid to a solution of the sulphate; the *methiodide*, B, MeI, m. p.  $275^\circ$  (decomp.), forms large, prismatic crystals containing water of crystallisation. On heating with acetic anhydride, isoBebeerine yields (1)  *$\alpha$ -hydroxy-triacetylisoBebeerine*, m. p.  $130$ – $140^\circ$ ,  $[\alpha]_D^{20} + 68.1^\circ$  in pyridine, which is colourless and amorphous, and  *$\beta$ -hydroxytriacetylisoBebeerine*, m. p.  $291^\circ$  (approx.),  $[\alpha]_D = 0^\circ$ , which crystallises in colourless needles and is only soluble in pyridine. On hydrolysis by sodium hydroxide in alcohol, each triacetyl derivative yields a corresponding *hydroxymonoacetylisoBebeerine*; the  $\alpha$ -compound, m. p.  $280^\circ$  (approx.), crystallises in colourless, slender needles, and the  $\beta$ -isomeride, m. p.  $332^\circ$  (approx.), forms microscopic needles. Both are insoluble, except in solutions of the alkali hydroxides. *BenzoylisoBebeerine*, m. p.  $215^\circ$  (approx.), obtained by the action of benzoic anhydride on isoBebeerine, crystallises from alcohol in glaucous, yellow leaflets.

$\beta$ -Bebeerine,  $C_{18}H_{21}O_3N$ , is amorphous, but yields a crystalline *methiodide*, B, MeI, m. p.  $80^\circ$  (hydrated) or  $258$ – $259^\circ$  (dry, decomp.). Both bebeerine and  $\beta$ -bebeerine on heating with acetic anhydride yield the same *hydroxytriacetylbebeerine*,  $C_{24}H_{29}O_7N$ , m. p.  $125$ – $135^\circ$ , which is amorphous, and loses two acetyl groups on treatment with potassium hydroxide in alcohol.

T. A. II.

**Zygadenine, the Crystalline Alkaloid of Zygadenus intermedius.** FREDERICK W. HEYL, F. E. HEPNER, and SYLVESTER K. LOY (*J. Amer. Chem. Soc.*, 1913, 35, 258–262).—It has been shown already (A., 1911, ii, 325) that the leaves of *Zygadenus intermedius* yield 0.3–0.4% of a mixture of alkaloids. Further work on this subject has resulted in the isolation of a pure alkaloid, *zygadenine*,  $C_{26}H_{33}O_{10}N$ , m. p.  $200$ – $201^\circ$ ,  $[\alpha]_D - 48.2^\circ$ , which crystallises from benzene in clusters of lustrous needles, and from alcohol in orthorhombic prisms containing  $2H_2O$ ; the *aurichloride* forms long, dense prisms. The alkaloid gives a yellowish-orange coloration with concentrated sulphuric acid, changing to a brilliant cherry-red. Its physiological action resembles that of veratrine.

E. G.

**Electrochemical Reductions. III. Reduction of Nitrosoamines.** HILMAR JOHANNES BACKER (*Rec. trav. chim.*, 1913, 32, 39–47. Compare A., 1912, i, 339, 730).—Nitrosopiperidine suspended in sulphuric acid (10%) was electrolysed at a cathode of tinned copper when an 81% yield of the corresponding hydrazine (estimated by oxidation to the tetrazone) was obtained (compare Knorr, A., 1884, 467; Abrens, A., 1897, i, 369). At a platinum electrode, the hydrogen was incompletely utilised, and the yield of hydrazine sank to 32%. An excess of hydrogen was found to be practically without effect on the hydrazine.

Diaminopiperazine was obtained in 55% yield by the action of zinc

dust and acetic acid on dinitrosopiperazine (compare Schmidt and Wichmann, A., 1892, 210). Electrolytic reduction at a tinned copper cathode of a suspension of the latter in a mixture of acetic and sulphuric acids gave a 38% yield of diaminopiperazine, which, however, increased to 72% when the mixture of acids was replaced by an aqueous solution of sodium sulphate to which a few drops of sulphuric acid had been added. An attempt to convert dinitrosopiperazine into dinitropiperazine by the action of nitric acid was unsuccessful.

Phenylmethylhydrazine (compare Fischer, A., 1878, 312; 1887, 135) was formed by electrolytic reduction of phenylmethylnitrosoamine suspended in dilute acetic acid at a tinned copper cathode. The yield was 79% of the theoretical.

$\alpha$ -Nitroso- $\alpha$ -methylcarbamide,  $\text{NH}_2\text{CO}\cdot\text{NMe}\cdot\text{NO}$ , was readily reduced in sulphuric acid suspension at a tin cathode with the formation of methylsemicarbazide (compare Brüning, A., 1890, 23; Young and Oates, T., 1901, 79, 662), which was identified by conversion into benzylidenemethylsemicarbazone, white needles, m. p. 163°. Young and Oates (*loc. cit.*) give 159–160° as m. p. of this substance, whilst Michaelis and Hadanek (A., 1908, i, 1020) found 162°. II. W.

**Indole.** RUDOLF WEISSGERBER (*Ber.*, 1913, 46, 651–659).—The difficulty experienced in preparing derivatives of indole is chiefly due to the lability of the imino-hydrogen atom. If this atom is replaced by a group which can be subsequently removed, it is found possible to obtain halogen derivatives by direct substitution and to disrupt the indole ring so that anthranilic acid results.

[With ARNO KLEMM].—Halogens react violently with indole, and only by working in very dilute solutions could Pauly and Gundermann obtain iodoindole (A., 1909, i, 71). When 1-benzoylindole (A., 1911, i, 155), however, is treated in the cold with bromine in carbon disulphide, *bromo-1-benzoylindole*,  $\text{C}_{15}\text{H}_{11}\text{ONBr}$ , is obtained in thick plates, m. p. 97–98°, which may be hydrolysed by dilute ammonia or, more conveniently, by means of sodium ethoxide in alcoholic solution, when water precipitates *bromoindole*,  $\text{C}_8\text{H}_7\text{NBr}$ , in silvery leaflets which have a strong faecal odour and undergo vigorous decomposition at 67°. The compound is not very stable, but the bromine atom resists the action of alkalis.

1-Benzoylindole also combines with chlorine, and the *chloro-1-benzoylindole*, colourless prisms, m. p. 97–99°, may be hydrolysed to the chloroindole which Mazzara and Borgo obtained by the action of sulphuryl chloride on indole (A., 1906, i, 304). Since the benzoyl derivatives may be oxidised to benzoylanthranilic acid, the halogen is present in the pyrrole ring, and, from their similarity to Pauly's 3-iodoindole, the constitution of which was satisfactorily determined, the conclusion is drawn that the bromo- and chloro-derivatives are also substituted in position 3, although all three compounds give 2-oxindole when treated with dilute acids.

[With O. HERZ].—The oxidation of indole itself results in the formation of amorphous masses, but the benzoyl compound is readily converted by permanganate in acetone solution into benzoylanthranilic acid, and this, by hydrolysis, into anthranilic acid itself.

[With F. KRAFT.]—The conversion of an indole derivative into indigotin has been accomplished by passing ozone through a strongly alkaline solution of 3-indolecarboxylic acid (A., 1911, i, 155). The reaction commences quickly, but the yield is only about 38%, anthranilic acid being isolated from the by-products. Other oxidising agents do not yield indigotin, neither does 2-indolecarboxylic acid give rise to that dye.

J. C. W.

**Preparation of Substituted Indoles by the Catalytic Decomposition of Hydrazones.** ALEXANDER E. ARBUZOV and V. M. TICHVINSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 70—74).—When heated with cuprous chloride or bromide, or platinum or zinc chloride, hydrazones of aldehydes and ketones undergo catalytic decompositions in directions depending on their structures and on the magnitudes of the radicals present. In the cases already investigated, the principal products are substituted indole derivatives.

Methyl-ethyl ketone-phenylhydrazone (50 grams), when heated at 180—230° in presence of cuprous chloride (0.1 gram), yields 2:3-dimethylindole, the yield being about 60%.

Similarly, propaldehydephenylhydrazone gives skatole in 73—74% yield, whilst propaldehydetolylhydrazone gives 3:5-dimethylindole,  $C_{10}H_{11}N$ , which crystallises in feathery masses of colourless, silky needles, m. p. 74—74.5°.

T. H. P.

**5, 6-, and 8-Iodoquinolines and Their Derivatives.** JOHANN HOFWITZ, HEDWIG FRAENKEL, and ELSE SCHROEDER (*Annalen*, 1913, 396, 53—75).—8-Aminoquinoline is obtained by the reduction of 8-nitroquinoline best by iron and acetic acid. When tin or stannous chloride and hydrochloric acid are used, the resulting 8-aminoquinoline is contaminated with 5-chloro-8-aminoquinoline. 8-Iodoquinoline,  $C_8H_6I$ , m. p. 36°, colourless needles, prepared from diazotised 8-aminoquinoline in the usual manner, forms a *platinichloride*,

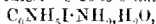


m. p. 251°, orange needles, and *methiodide*, m. p. 200°, yellow needles. By oxidation with alkaline potassium ferricyanide, the latter yields

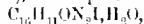
8-iodo-1-methyl-2-quinolone,  $C_8H_5I$   $\begin{matrix} \text{NMe} \cdot \text{CO} \\ | \\ \text{CH} = \text{CH} \end{matrix}$  m. p. 168°.

The 8-iodoquinoline, m. p. 136°, described by Claus and Grau in 1893, is 5-chloro-8-iodoquinoline, produced from the impure 8-aminoquinoline mentioned above.

8-Iodoquinoline is readily nitrated by concentrated sulphuric acid and nitric acid (D 1.5) in the cold, yielding 8-iodo-5-nitroquinoline, m. p. 192°, pale yellow needles. 8-Iodo-5-aminoquinoline,



m. p. 148° (anhydrous, 155°), brown prisms (*benzoyl* derivative,

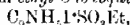


m. p. 218°, leaflets), yields 5:8-di-iodoquinoline, m. p. 162°, and 5-chloro-8-iodoquinoline, m. p. 138°, by the usual methods.

By the Sandmeyer process, 5-aminoquinoline yields 5-chloroquinoline, m. p. 44—45° (Claus and Jungmann give 31°), the nitration of which

produces 5-chloro-8-nitroquinoline, m. p. 136° (184°, Claus and Jungmanns). 5-Chloro-8-aminoquinoline, m. p. 75° (69°, Claus and Jungmanns), forms an *acetyl* derivative, m. p. 140°, and is converted into 5-chloro-8-iodoquinoline by the usual method.

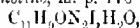
8-Iodoquinoline is readily attacked by 40% fuming sulphuric acid in the cold, yielding 8-iodoquinoline-5-sulphonic acid,  $C_9NH_5I \cdot SO_3H$ , silver grey leaflets, of which the sodium and barium salts are described. The silver salt,  $C_9NH_5I \cdot SO_3Ag \cdot \frac{1}{2}H_2O$ , when dehydrated, reacts with methyl iodide at 120—130° to form chiefly the *betaine*, m. p. 292° (decomp.), of 8-iodo-1-methylquinoline 5-sulphonic acid, and with ethyl iodide at 130—140° to form *ethyl 8-iodoquinoline-5-sulphonate*,



m. p. 156°, colourless leaflets, and the *betaine*, m. p. about 340° (decomp.), of 8-iodo-1-ethylquinoline 5-sulphonic acid. Sodium 8-iodoquinoline-5-sulphonate and phosphorus pentachloride at 125—130° yield 8-iodoquinoline-5-sulphonyl chloride, m. p. 116°, yellow needles or prisms, from an ethereal solution of which and dry ammonia the *sulphonamide*,  $C_9NH_5I \cdot SO_2 \cdot NH_2$ , m. p. 212°, is obtained. The position of the sulpho-group in 8-iodoquinoline-5-sulphonic acid is proved by nitration, whereby the sulpho- is replaced by the nitro-group, and 8-iodo-5-nitroquinoline, m. p. 192°, is obtained.

5-Iodoquinoline methiodide is oxidised to 5-iodo-1-methyl-2-quinoline, m. p. 172°, yellow leaflets, by alkaline potassium ferricyanide. 5-Iodo-8-nitroquinoline, m. p. 160°, yellow needles, obtained by the nitration of 5-iodoquinoline on the water-bath, yields by reduction 5-iodo-8-aminoquinoline, m. p. 122°, brown needles (*benzoyl* derivative, m. p. 161°), from which 5:8-di-iodoquinoline, m. p. 161°, and 8-chloro-5-iodoquinoline, m. p. 118°, are prepared by the usual methods; the formation of the di-iodo compound determines the orientation of the nitro-group in nitrated 5-iodoquinoline.

The following derivatives of 6-iodoquinoline have been prepared: 6-iodo-1-methyl-2-quinoline,  $C_{10}H_8ON$ , m. p. 129°, yellow needles or leaflets; 6-iodo-5-aminoquinoline, m. p. 176° (*acetyl* derivative,

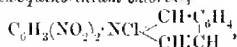


m. p. 197°); 5:6-di-iodoquinoline, m. p. 125°, and 5-chloro-6-iodoquinoline, m. p. 141°.

C. S.

2-*op*-Dinitrophenylisoquinolinium Chloride and its Products of Transformation. THEODOR ZINCKE and G. WEISSFENNING (*Annalen*, 1913, 396, 103—131).—The authors' experiments have not realised their expectations that the action of arylamines or of cyanogen bromide on 2-*op*-dinitrophenylisoquinolinium chloride would yield the glutacondialdehyde derivative,  $CHO \cdot C_6H_4 \cdot CH_2 \cdot CHO$ , or colour bases,  $Na \cdot CH \cdot C_6H_4 \cdot CH \cdot CH \cdot NHAr$ , analogous to those obtained in the pyridine series (*A.*, 1901, i, 448, 921; 1905, i, 467, 923; 1907, i, 625).

2-*op*-Dinitrophenylisoquinolinium chloride,



decomp. 130°, stout, rhombic crystals, is obtained by keeping an ethereal solution of isoquinoline and 1-chloro-2:4-dinitrobenzene for

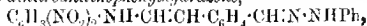
several weeks or months at the ordinary temperature. It forms a *platinichloride*, m. p. 222°, and *periodide*,  $C_{15}H_{10}O_4N_3I_2$ , dark brown needles, and is readily hydrolysed by hot aqueous sodium nitrite, yielding *isoquinoline*, hydrogen chloride, and 2:4-dinitrophenol (in the form of the dinitrophenylisoquinolinium and *isoquinoline* salts; the latter has m. p. 127°). Hydrogen sulphide decomposes the chloride, 2:4-dinitrobenzyl mercaptan being produced in the aqueous solution and 2:4-dinitrophenyl sulphide in alcoholic solution.

Dinitrophenylisoquinolinium chloride is converted by aqueous ammonia or sodium carbonate or by an aqueous solution of methylamine or aniline, less satisfactorily by aqueous sodium hydroxide, into the  $\psi$  base,  $C_6H_3(NO_2)_2 \cdot N < \begin{smallmatrix} CH(OH) \cdot C_6H_4 \\ CH=CH \end{smallmatrix}$ , orange-red needles, m. p. 141–142°, darkening at about 90°, which is reconverted into dinitrophenylisoquinolinium chloride by dilute hydrochloric acid, and yields ethers,  $C_6H_3(NO_2)_2 \cdot N < \begin{smallmatrix} CH(OR) \cdot C_6H_4 \\ CH=CH \end{smallmatrix}$ , by warming with alcohols; the *methyl ether*, m. p. 149°, dark red crystals, *ethyl ether*, m. p. 135°, pale red prisms, and *isobutyl ether*, m. p. 122°, orange-red crystals, have been prepared. These ethers, which are also produced directly from dinitrophenylisoquinolinium chloride and ammonia dissolved in the alcohol, are converted one into another by warming with the necessary alcohol.

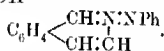
By heating with water at 90–95° for some hours, or with acetone at 100°, or with boiling acetic anhydride, the freshly precipitated  $\psi$ -base is converted into an *isomeride*, m. p. 151°, dark red crystals with a violet shimmer. The isomeride is only slowly attacked by warm dilute hydrochloric acid, does not form ethers by boiling with alcohols, and is slowly converted into dinitrophenylisoquinolinium chloride by hot concentrated hydrochloric acid. It does not react with phenylhydrazine, and is, therefore, not the aldehydo-base,  $CHO \cdot C_6H_4 \cdot CH : CH \cdot NH \cdot C_6H_3(NO_2)_2$ ; probably it has the constitution  $NHR \cdot CH : CH \cdot C_6H_4 \cdot CH(OH) \cdot O \cdot CH < \begin{smallmatrix} NR-CH \\ C_6H_4 \cdot CH \end{smallmatrix}$  [where R is  $C_6H_3(NO_2)_2$ ], and is formed by the union of the  $\psi$ -base and the aldehydo-base.

When boiled in alcoholic solution with aniline or *p*-toluidine, dinitrophenylisoquinolinium chloride or, better, the  $\psi$ -base or the violet isomeride is decomposed into 2:4-dinitroaniline and the 2-arylisoquinolinium chloride. 2-*Phenylisoquinolinium chloride*,  $C_{17}H_{12}NCl \cdot 2H_2O$ , long needles, forms a *platinichloride*, m. p. 228–229°, orange needles, and *mercurichloride*, m. p. 183–184°; the *dichromate*, decomp. about 195°, and *picrate*, m. p. 136–137°, yellow needles, are described. 2-*p-Tolylisoquinolinium chloride*,  $(C_{16}H_{11}NCl \cdot 2H_2O)$ , colourless needles, forms a *platinichloride*, m. p. 216–217°, orange-yellow needles.

Dinitrophenylisoquinolinium chloride is converted into the  $\psi$ -base by hydrazine hydrate, but reacts with phenylhydrazine in boiling alcohol just as does dinitrophenylpyridinium chloride (A., 1904, i, 448), yielding the *dinitroanilinophenylhydrazone*,



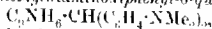
m. p. 183—184°, black needles. In a similar manner the *dinitro-anilino-p-tolylhydrazones*,  $C_{22}H_{16}O_4N_6$ , m. p. 185—186°, black leaflets with a red shimmer, and the *dinitroanilino-phenylmethylhydrazones*,  $C_{20}H_{14}O_4N_6$ , m. p. 181—182°, reddish-brown leaflets, have been obtained. These three substances are decomposed by boiling alcohol and hydrochloric acid, D 1.19, into 2,4-dinitroaniline and 2-anilinoisoquinolinium chloride,  $C_9H_7N(NHPh)Cl$ , m. p. 198—200°, faintly yellow, monoclinic prisms (*platinichloride*, m. p. 190° [decomp.]), 2-p-toluidinoisoquinolinium chloride, rhombic plates, and 2-methylanilinoisoquinolinium chloride, faintly yellow needles (*picrate*, m. p. 170°; *platinichloride*, m. p. 185°; *mercurichloride*, m. p. 174°), respectively. 2-Anilinoisoquinolinium chloride yields isoquinoline (aniline could not be detected) by reduction with zinc dust and dilute hydrochloric acid, and by treatment with aqueous sodium hydroxide, sodium carbonate, or ammonia yields a red precipitate which is apparently a mixture of the  $\psi$ -base,  $C_6H_4 \begin{smallmatrix} \text{CH(OH) \cdot N \cdot NHPh} \\ \text{CH} \end{smallmatrix}$ , and the azo-compound,



C. S.

**Bromination of 6-Methylquinoline and 6-Quinolinealdehyde.** JOHANN HOWITZ and J. PHILIPP (*Annalen*, 1913, 396, 23—37).—The dibromide of 6-methylquinoline hydrobromide is obtained as a brick-red, crystalline powder by saturating a cold chloroform solution of 6-methylquinoline with hydrogen bromide and subsequently adding bromine (1 mol.). By carefully heating it at 170—180° for two hours, cooling to 140°, and adding more bromine (1 mol.), and heating again at 170—180° for two hours, the substance is converted into 6-dibromomethylquinoline,  $C_9H_7CHBr_2$ , m. p. 159—160°, white needles (*platinichloride*,  $2C_9H_7NBr_2 \cdot H_2PtCl_6$ , m. p. 235°, orange crystals), and 5-bromo-6-dibromomethylquinoline,  $C_{10}H_6NBr_3$ , m. p. 141°, yellowish-white needles, each of which loses two atoms of bromine by hydrolysis with alcoholic potassium hydroxide.

By boiling with water for ten to fifteen minutes and basifying, 6-dibromomethylquinoline is converted into 6-quinolinealdehyde,  $C_{10}H_7ON$ , glistening needles containing  $H_2O$ , m. p. 55° (anhydrous, 75—76°), which exhibits the usual reducing and additive properties of an aldehyde. It yields quinoline 6-carboxylic acid by oxidation, forms a *platinichloride*,  $2C_9H_7ON \cdot H_2PtCl_6$ , m. p. 244°, reddish-yellow needles, *albazine*,  $N_2(C_9H_7ON)_2$ , m. p. 261°, yellow needles, *semicarbazone*, m. p. 239°, *osazone*, m. p. 191°, *phenylhydrazone*, m. p. 185°, yellow crystals containing  $H_2O$ , *azil*,  $NPh \cdot CH \cdot C_9H_6$ , m. p. 99°, and *o-tolil*, m. p. 97°, and condenses with dimethylaniline in the presence of zinc chloride to form tetramethyldiaminodiphenyl-6-quinolylmethane,



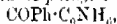
m. p. 160°, almost colourless needles, which yields a green dye by oxidation with lead peroxide. When heated with methyl iodide at 100°, 8-quinolinealdehyde yields a *methiodide*,  $CHO \cdot C_9H_6NMeI$ , m. p. 218°; the latter is oxidised by cold alkaline potassium ferricyanide to

1-methyl-2-quinolone-6-aldehyde,  $CHO \cdot C_9H_5 \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ | \\ \text{CH} = \text{CH} \end{smallmatrix}$ , m. p. 164°.

colourless needles, or the corresponding acid,  $C_{11}H_9O_3N$ , m. p. above  $300^\circ$ , according to the duration of the reaction.

3-Bromo-6-dibromomethylquinoline is hydrolysed by an excess of potassium carbonate and a little water at  $115-120^\circ$ , yielding 3 *bromoquinoline-6-aldehyde*, m. p.  $135^\circ$ , white needles (*aldazine*, m. p.  $194^\circ$ , pale yellow needles; *oxime*, m. p.  $217^\circ$ ; *phenylhydrazones*, m. p.  $185^\circ$ ; *anil*, m. p.  $124^\circ$ ), in which the position of the halogen is determined by its oxidation to 3-bromopyridine-5:6-dicarboxylic acid by hot alkaline potassium permanganate. By oxidation with chromic and sulphuric acids, the aldehyde yields 3-bromoquinoline-6-carboxylic acid, m. p.  $245^\circ$ , long white needles. C. S.

**8-Quinolyl Ketones and their Derivatives.** JOHANN HOWITZ and O. KOPKE (*Annalen*, 1913, 396, 38-52).—Hitherto, only quinolyl ketones have been known containing the carbonyl group attached to the pyridine nucleus. Bromoquinolines and 8-bromomethylquinoline do not react with magnesium in ether. The interaction of 8-quinolinealdehyde (Howitz and Schwenk, A, 1905, i, 471) and magnesium phenyl bromide in ether at  $0^\circ$ , leads to the formation of *phenyl 8-quinolylcarbinol*,  $OH \cdot CHPh \cdot C_8NH_6$ , m. p.  $104^\circ$ , large colourless plates, in about 60% yield. The carbinol forms a *platinichloride*, m. p.  $198^\circ$  (decomp.), and a *benzoate*, m. p.  $146^\circ$ , and is oxidised by chromic and acetic acids on the water-bath to *phenyl 8-quinolyl ketone*,



m. p.  $94^\circ$ , colourless plates (*platinichloride*, m. p.  $213^\circ$  [decomp.]). By treatment with hydroxylamine hydrochloride and potassium hydroxide in boiling alcohol, the ketone yields an *oxime*,  $C_{10}H_{12}ON_2 \cdot H_2O$ , m. p.  $121^\circ$ , which is converted into an *isomeride*,  $C_{10}H_{12}ON_2 \cdot H_2O$ , m. p.  $165^\circ$ , by heating at  $120^\circ$ , and then crystallising from alcohol. By treating a cold ethereal solution of the oxime, m. p.  $121^\circ$ , with phosphorus pentachloride, and decomposing the precipitated imino-chloride with water at  $0^\circ$ , 8-benzoylaminoquinoline,  $C_8NH_6 \cdot NHBz$ , m. p.  $53^\circ$ , is obtained, the identity of which is established by its formation by the benzylation of 8-aminoquinoline and by its decomposition into 8-aminoquinoline and benzoic acid by concentrated hydrochloric acid at  $160^\circ$ . The oxime, m. p.  $121^\circ$ , is therefore anti-*phenyl*

8-quinolyl ketoxime,  $\begin{matrix} C_8NH_6 \cdot CPh \\ HO-N \end{matrix}$ . In a similar manner, the oxime, m. p.

$165^\circ$ , is proved to be syn-*phenyl 8-quinolyl ketoxime*,  $\begin{matrix} C_8NH_6 \cdot CPh \\ N(OH) \end{matrix}$ , by its conversion by the Beckmann transformation into the anilide of quinoline-8-carboxylic acid; unfortunately, neither the anilide nor the quinolinecarboxylic acid produced by its hydrolysis has been isolated, but only the aniline resulting in the latter operation.

Phenyl 8-quinolyl ketone forms a *phenylhydrazone*, m. p.  $190^\circ$ , *semicarbazone*, m. p.  $188^\circ$ , and *azine*,  $C_{12}H_{10}N_4$ , m. p.  $287^\circ$ .

8-Quinolylmethylcarbinol,  $OH \cdot CHMe \cdot C_8NH_6$ , m. p.  $65^\circ$  (*platinichloride*, m. p.  $197^\circ$  [decomp.], orange-yellow crystals; *benzoate*, m. p.  $100^\circ$ ), obtained ultimately from magnesium methyl iodide and 8-quinolinealdehyde in ether, is oxidised to 8-quinolyl methyl ketone,  $C_8NH_6 \cdot COMe$ , m. p.  $45^\circ$ , b. p. about  $295^\circ$ , by potassium dichromate

and very dilute sulphuric acid on the water-bath. The ketone forms a *semicarbazone*, m. p. 223°, and an *oxime*, m. p. 137°; the latter has only been obtained in one modification, which is *syn*-8-quinolyl methyl ketoxime, since it yields 8-acetylaminoquinoline by the Beckmann transformation.

8-*Quinolylethylcarbinol* (*platinichloride*, m. p. 216° [decomp.]; *benzozole*, m. p. 82°) and 8-*quinolyl ethyl ketone*, b. p. about 230° (*semicarbazone*, m. p. 203°), have been prepared by methods similar to the preceding.

C. S.

**Preparation of 9-Methylcarbazole.** FARBERWERK VORM. MEISTER, LEUCUS & BRÜNING (D.R.P. 255304).—The technically valuable 9-methylcarbazole can be prepared in about 70% yield by the following method.

Dry potassium carbazole is heated with freshly distilled ethyl chloroacetate during about three hours, yielding *ethyl carbazole-9-acetate*, m. p. 97°; this when hydrolysed with an alkaline hydroxide gives rise to *carbazole-9-acetic acid*, glistening, colourless leaflets, m. p. 215°, which, when carefully heated at 250—270°, evolves carbon dioxide and furnishes pure 9-methylcarbazole, m. p. 87°.

F. M. G. M.

**Kehrmann's Interpretation of Chromo-Isomeric Acridonium Salts as "Quinhydrone Salts" which Contain Hydroacridine.** ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 682—684. Compare this vol., i, 208).—Kehrmann's view that the dark green iodide obtained from methylphenazonium salts is a quinhydrone salt composed of one molecule of azonium tri-iodide and two molecules of methyl-dihydro-phenazine, is combated.

According to Kehrmann, the salt should be decomposed by water into phenylmethylacridonium iodide, phenylmethylhydroacridine, and hydrogen iodide, but in reality it gives a clear, neutral solution, and behaves as a normal binary electrolyte.

J. C. W.

**"Halochromism" of the Derivatives of Phenylisooxazolone and of the Indogenides.** ANDRÉ MEYER (*Compt. rend.*, 1913, **156**, 714—717. Compare Bayer and Villiger, *A.*, 1901, i, 658; 1902, i, 380, 769; Meyer, *A.*, 1912, i, 1019).—The indogenides and in particular the isooxazole-indogenides give coloured compounds with acids and metallic salts, comparable to the oxonium salts, and the author has prepared a number of such compounds.

On passing dry hydrogen chloride into a suspension of piperonylidene-isooxazolone in benzene at -10°, a deep red additive compound is formed and crystallises out.

Condensation products are also formed from the isooxazolones and stannic chloride, ferric chloride, or aluminium chloride, and a number of such stannichlorides, prepared by the addition of anhydrous stannic chloride to benzene solutions of the isooxazolones, are described.

*Phenylbenzylideneisooxazolone stannichloride*,  $C_{17}H_{11}O_2N_2SnCl_4$ , a yellow, microcrystalline powder, decomposes at 200°.

*Phenylpiperonylideneisooxazolone stannichloride*,  $C_{17}H_{11}O_3N_2SnCl_4$ , deep red leaflets, decomposes at 160°.



*Phenylanisylidenesooxazolone stannichloride*,  $C_{17}H_{13}O_3N_2SnCl_4$ , a deep yellow powder, decomposes at  $155^\circ$ .

*Phenyl-o-methoxybenzylidenesooxazolone stannichloride*,  
 $2C_{17}H_{13}O_3N_2SnCl_4$ ,  
 an orange powder, decomposes at  $150^\circ$ .

*Phenylcavullylidenesooxazolone stannichloride*,  $C_{17}H_{13}O_4N_2SnCl_4$ , a brownish-red, microcrystalline powder, decomposes at  $150^\circ$ .

*Phenyldimethylaminobenzylidenesooxazolone stannichloride*,  
 $C_{18}H_{16}O_3N_2 \cdot 2SnCl_4$ ,  
 a bright red powder, decomposes above  $250^\circ$ .

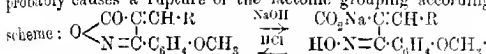
The indogenides furnish similar compounds, such as *piperonylidenehydroxythionaphthen stannichloride*,  $C_{15}H_{10}O_3S_2SnCl_4$ , a violet-black, microcrystalline powder, decomposing at  $230^\circ$ .

All these substances are hydrolysed by water and are practically insoluble in organic solvents, their colours being deeper than those of the parent substances.

The mixed azo-derivatives of phenylisooxazolone are also "halochromes" and give coloured stannichlorides, the one described being *benzenearophenylisooxazolone stannichloride*,  $C_{15}H_{11}O_2N_2 \cdot SnCl_4$ , an orange-yellow powder, decomposing at  $150^\circ$ .  
 W. G.

**Some Derivatives of the Methoxyphenylisooxazolones.**  
 ANDRÉ WAHL and C. SILBERZWEIG (*Bull. Soc. chim.*, 1913, [iv], 13, 236—240. Compare Wahl and Meyer, A., 1908, i, 368; Wahl, *ibid.*, 1909, i, 260).—The authors have condensed *o*-, *m*-, and *p*-methoxyphenylisooxazolone with a number of aldehydes, and have thus prepared the following substances: 3-*o*-methoxyphenyl-4-benzylidenesooxazolone, yellow leaflets, m. p.  $150^\circ$ ; 3-*m*-methoxyphenyl-4-benzylidenesooxazolone, yellow needles, m. p.  $110^\circ$ ; 3-*p*-methoxyphenyl-4-benzylidenesooxazolone, yellow leaflets, m. p.  $170^\circ$ ; 3-*o*-methoxyphenyl-4-anisylidenesooxazolone, pale yellow, m. p.  $154^\circ$ ; 3-*m*-methoxyphenyl-4-anisylidenesooxazolone, yellow crystals, m. p.  $161^\circ$ ; 3-*p*-methoxyphenyl-4-anisylidenesooxazolone, pale yellow leaflets, m. p.  $165^\circ$ ; 3-*o*-methoxyphenyl-4-cinnamylidenesooxazolone, orange-yellow, m. p.  $163^\circ$ ; 3-*m*-methoxyphenyl-4-cinnamylidenesooxazolone, orange-yellow, m. p.  $146$ — $147^\circ$ ; 3-*p*-methoxyphenyl-4-cinnamylidenesooxazolone, orange needles, m. p.  $163^\circ$ ; 3-*o*-methoxyphenyl-4-furfurylidenesooxazolone, yellow crystals, m. p.  $171$ — $172^\circ$ ; 3-*p*-methoxyphenyl-4-furfurylidenesooxazolone, yellow needles, m. p.  $141$ — $142^\circ$ ; 3-*o*-methoxyphenyl-4-*p*-dimethylaminobenzylidenesooxazolone, red needles, m. p.  $190^\circ$ ; 3-*m*-methoxyphenyl-4-*p*-dimethylaminobenzylidenesooxazolone, red needles, m. p.  $146^\circ$ ; 3-*p*-methoxyphenyl-4-*p*-dimethylaminobenzylidenesooxazolone, red leaflets, m. p.  $192^\circ$ ; 3-*o*-methoxyphenyl-4-*o*-hydroxybenzylidenesooxazolone, yellow leaflets, m. p.  $195^\circ$ ; 3-*o*-methoxyphenyl-4-*p*-hydroxybenzylidenesooxazolone, orange-yellow, m. p.  $218^\circ$ ; 3-*m*-methoxyphenyl-4-*p*-hydroxybenzylidenesooxazolone, yellow leaflets, m. p.  $215^\circ$ ; 3-*p*-methoxyphenyl-4-*p*-hydroxybenzylidenesooxazolone, golden-yellow needles, m. p.  $204$ — $205^\circ$ ; 3-*o*-methoxyphenyl-4-*p*-hydroxy-*m*-methoxybenzylidenesooxazolone, yellow crystals, m. p.  $168^\circ$ ; 3-*o*-methoxyphenyl-4-*p*-hydroxy-*m*-methoxybenzylidenesooxazolone, orange-yellow crystals, m. p.  $203^\circ$ ; 3-*p*-methoxyphenyl-4-*p*-hydroxy-*m*-methoxybenzylidenesooxazolone, yellow crystals, m. p.  $199^\circ$ ; 3-*o*-methoxyphenyl-

4 *mp*-dihydroxybenzylidenesooxazolone, orange crystals, *m. p.* 209°; 3-*m*-methoxyphenyl-4-*mp*-dihydroxybenzylidenesooxazolone, orange-red needles, *m. p.* 184°; 3-*p*-methoxyphenyl-4-*mp*-dihydroxybenzylidenesooxazolone, orange crystals, *m. p.* 193°; with *o*-vanillin, the 3-*o*- and *p*-methoxyphenylisooxazolones form yellow leaflets, *m. p.* 195°, and orange-yellow leaflets, *m. p.* 208°, respectively, whilst with resorcyaldehyde, 3-*o*-, *m*- and *p*-methoxyphenylisooxazolones yield orange-yellow crystals, *m. p.* 235°, orange-yellow crystals, *m. p.* 240°, and yellow crystals, *m. p.* 209°, respectively. The phenolic derivatives dissolve in alkali, forming solutions in which the colour varies from yellow to reddish-violet. Presence of excess of alkali rapidly discharges these colorations, yielding colourless solutions from which acids re-precipitate the original substance. The action of excess of alkali probably causes a rupture of the lactonic grouping according to the



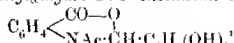
The three methoxyphenylisooxazolones have been condensed with 5-bromoisatin chloride, yielding the three 3-methoxyphenylisooxazolone-5-bromo-2-indoles,  $\text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3 \begin{array}{c} \diagup \\ \text{O} \end{array} \text{CO} > \text{C} \cdot \text{C} \begin{array}{c} \diagdown \\ \text{NH} \\ \diagup \\ \text{CO} \end{array} \text{C}_6\text{H}_4\text{Br}$ , the proper-

ties of which are similar to those of the previously described indigoid dyes derived from the three methoxyphenylisooxazolones and isatin chloride. If, however, sodium hyposulphite is added to their solution in alkali, the yellow colour of the latter persists. Addition of acid causes the formation of a flocculent, yellow precipitate. The latter dissolves in alcohol, forming a red solution, the colour of which deepens on addition of an oxidising agent, the initial dye being ultimately formed. The yellow precipitate appears to be the leuco-derivative of the dye. It presents no marked affinity for the textile fibres.

H. W.

**Action of Acetic Anhydride on some Benzylideneanthranilic Acids.** II. JOHN B. EKELEY and STILES CLINTON (*J. Amer. Chem. Soc.*, 1913, 35, 282—284).—Ekeley and Dean (A., 1912, i, 211) have shown that a series of oxazines can be obtained by the action of acetic anhydride on benzylideneanthranilic acids. The reaction seems to be of general application, and further compounds are now described.

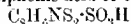
*Protocatechylidenanthranilic acid*, *m. p.* 204°, obtained by the condensation of protocatechualdehyde with anthranilic acid, forms orange-red crystals, and is converted by acetic anhydride into 4-acetyl-3-(3':4')-dihydroxyphenyl-2-hydro-2:4-benzoxazine-1-one,



*m. p.* 121°. *Bromosalicylideneanthranilic acid*, *m. p.* 198°, crystallises in yellow needles, and furnishes 4-acetyl-3-(4':2')-bromohydroxyphenyl-2-hydro-2:4-benzoxazine-1-one, *m. p.* 170°. *o*-Nitrobenzylidenanthranilic acid, *m. p.* 67°, forms straw-coloured needles, and yields 4-acetyl-3-*o*-nitrophenyl-2-hydro-2:4-benzoxazine-1-one, *m. p.* 167.5°. *o*-Methoxybenzylidenanthranilic acid, *m. p.* 122°, gives 4-acetyl-3-*o*-methoxyphenyl-2-hydro-2:4-benzoxazine-1-one, *m. p.* 165°. *Resorcyldenanthranilic acid* begins to

decompose at about  $150^{\circ}$ ; 4-acetyl-3-(1:3)-dihydroxyphenyl-dihydro-2:4-benzoxazine-1-one has m. p.  $192^{\circ}$ . p-Dimethylaminobenzylidene-anthranilic acid, m. p.  $176^{\circ}$ , yields 4-acetyl-3-p-dimethylaminophenyl-dihydro-2:4-benzoxazine-1-one, m. p.  $162^{\circ}$ . E. G.

**A Gelatinous Mercury Salt of an Organic Sulphonic Acid.** W. DÜMLE and BERTHOLD RASSOW (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 71—74).—By the action of fuming sulphuric acid on benzothiazole-methenesulphide, a monosulphonic acid of the composition:

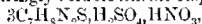


is obtained. When aqueous solutions of the potassium salt and of mercuric chloride are mixed together, a yellow solution is obtained, which, sooner or later, depending on the concentration, solidifies to a jelly. The jelly-forming substance is the normal mercuric salt, and its activity is such, that even in  $N/100$ -solution it is capable of producing a jelly at the ordinary temperature. The mercury salt is unstable, and the jellies sooner or later become cloudy in consequence of the formation of the basic salt,  $Hg(C_8H_6NS_2SO_3)_2 \cdot HgO$ , which separates out in the form of very small crystals. The stability of the jellies increases with the concentration of the mercury salt and those prepared from  $N/5$ -solutions of the potassium salt and mercuric chloride can be kept for some time before they begin to exhibit opalescence as a result of the initial precipitation of the basic salt.

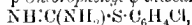
The colloidal mercury salt is coagulated by electrolytes and alcohol, the coagulum being converted into the crystalline basic salt on contact with water.

From the examination of freshly prepared solutions of the mercury salt, it has been found that the viscosity increases with time, the rate of increase varying very considerably from one solution to another even when the conditions under which the solutions were prepared, were exactly the same. Most electrolytes increase the viscosity, but potassium iodide increases it to a remarkable extent. H. M. D.

**Aromatic  $\psi$ -Thiocarbamides and Orthothiocarbonic Esters.** FRITZ ARNDT (*Annalen*, 1913, 396, 1—22. Compare A., 1911, i, 918).—*Phenyl  $\psi$ -thiocarbamide*,  $NH_2C(NH_2) \cdot SPh$ , m. p.  $96-97^{\circ}$  (decomp.), glistening needles, prepared from phenyl mercaptan and cyanamide, forms a sparingly soluble *nitrate-sulphate*,



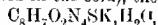
m. p.  $206^{\circ}$  (decomp.), which, however, is distinctly more soluble than the nitrate-sulphate of *p*-tolyl- $\psi$ -thiocarbamide (*loc. cit.*); in fact, the salts of phenyl- $\psi$ -thiocarbamide are much more soluble than those of the *p*-tolyl homologue. p-Chlorophenyl- $\psi$ -thiocarbamide,



forms a *nitrate-sulphate*,  $3C_6H_4N_2S_2H_2SO_4 \cdot HNO_3$ , m. p.  $222^{\circ}$  (decomp.).

The substance previously described as nitroso-*p*-tolyl- $\psi$ -thiocarbamide (*loc. cit.*) is now shown to be the *p*-tolyl- $\psi$ -carbamide salt of dinitroso-*p*-tolyl- $\psi$ -thiocarbamide,  $OH \cdot N \cdot N \cdot C(S_2H_2) \cdot N \cdot NO$ . The salt is decomposed by cold glacial acetic acid into nitrogen and *p*-tolyl thiocyanate, and by cold concentrated hydrochloric acid into nitrous acid and *p*-tolyl- $\psi$ -thiocarbamide. The yellow substance obtained by

its decomposition by boiling methyl alcohol receives the constitution  $C_6H_4S \cdot CO \cdot N \cdot NOH$ , since it yields *p*-tolylthiocyanate and mercaptan by treatment with concentrated hydrochloric acid. By gradually adding the *p*-tolyl- $\psi$ -thiocarbamide salt of dinitroso-*p*-tolyl- $\psi$ -thiocarbamide to a gently boiling methyl-alcoholic solution of potassium acetate (saturated in the cold), the potassium salt,



of the dinitroso-derivative is obtained. It crystallises in glistening needles, yields the calcium, barium, and ferric salts by double decomposition, and the benzamidine salt, white leaflets, by treatment with aqueous benzamidine hydrochloride, and by the action of dilute acetic acid yields the free dinitroso-compound, which, however, instantly decomposes into nitrous acid and nitroso-*p*-tolyl- $\psi$ -thiocarbamide,



decomp.  $115-120^\circ$ , golden-yellow leaflets. The latter yields nitrous acid and *p*-tolyl- $\psi$ -thiocarbamide by treatment with concentrated hydrochloric acid, and nitrogen and *p*-tolyl thiocyanate with warm glacial acetic acid. By treatment with sodium nitrite and hydrochloric acid, phenyl- $\psi$ -thiocarbamide and *p*-chlorophenyl- $\psi$ -thiocarbamide each yield  $\psi$ -thiocarbamide salts of the dinitroso- $\psi$ -thiocarbamide.

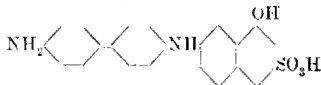
As mentioned previously (*loc. cit.*), *p*-tolyl ortho-thiocarbonate is obtained by treating a methyl-alcoholic solution of the *p*-tolyl- $\psi$ -thiocarbamide salt of dinitroso-*p*-tolyl- $\psi$ -thiocarbamide with aqueous ammonia. This reaction could not be explained when the *p*-tolyl- $\psi$ -thiocarbamide salt was considered to be a nitroso-compound. Its course is now clear. The ammonia liberates *p*-tolyl- $\psi$ -thiocarbamide and converts it into *p*-tolyl mercaptan, which then reacts with the dinitroso-compound (or its ammonium salt) in accordance with the equation:  $C_8H_7S \cdot C(N \cdot NO) \cdot N \cdot N \cdot OH + 3C_8H_7 \cdot SH = C(S \cdot C_8H_7)_4 + 2N_2 + 2H_2O$ . The orthothiocarbonate is also obtained by treating a methyl-alcoholic solution of the *p*-tolyl- $\psi$ -thiocarbamide salt or the potassium salt of dinitroso-*p*-tolyl- $\psi$ -thiocarbamide directly with *p*-tolyl mercaptan.

Phenyl orthothiocarbonate,  $C(SPh)_4$ , m. p.  $159^\circ$ , small leaflets, and *p*-chlorophenyl orthothiocarbonate,  $C(S \cdot C_6H_4Cl)_4$ , m. p.  $212-213^\circ$ , are prepared by methods similar to the preceding. *p*-Chlorophenyl orthothioformate,  $CH(S \cdot C_6H_4Cl)_3$ , m. p.  $111-112^\circ$ , almost colourless leaflets, is obtained by boiling *p*-chlorophenyl mercaptan in aqueous sodium hydroxide with an excess of chloroform. Phenyl tri-*p*-chlorophenyl orthothiocarbonate,  $SPh \cdot C(S \cdot C_6H_4Cl)_3$ , small, white leaflets, m. p. about  $181^\circ$ , obtained by warming potassium dinitrosophenyl- $\psi$ -thiocarbamide and the calculated amount of *p*-chlorophenyl mercaptan in methyl alcohol, is converted by crystallisation from acetic acid into a mixture of the tetraphenyl and the tetra-*p*-chlorophenyl esters of orthothiocarbonic acid; the latter has been isolated. Tri-*p*-chlorophenyl-*p*-tolyl orthothiocarbonate, m. p. about  $193^\circ$ , is prepared in a similar manner, and also tends to change to the unmixed esters. By reduction with boiling glacial acetic acid and zinc dust, it is converted into di-*p*-chlorophenyl-*p*-tolyl orthothioformate,  $C_6H_4S \cdot CH(S \cdot C_6H_4Cl)_2$ , m. p.  $96-97^\circ$ , white leaflets, which is not changed by crystallisation from glacial acetic acid.

C. S.

Preparation of 6-Aminodiaryl-amino- and 7-Aminodiaryl-amino-1-naphthol-3-sulphonic Acids with their Derivatives, FARRENFAHRKEN VORM, FRIEDR. BAYER & Co. (D.R.-P. 254510).—Numerous compounds obtained by the condensation of aromatic benzenoid amines with aminonaphthols in the presence of sodium hydrogen sulphite have been previously described (A., 1905, i, 585), and the reaction has now been extended to the diphenyl series.

4'-Amino-7-diphenylamino-1-naphthol-3-sulphonic acid (announced formula) is obtained when 1:7 dihydroxynaphthalene-3-sulphonic acid (240 parts) is boiled during forty-eight hours with benzidine (184 parts) and an aqueous solution of sodium hydrogen sulphite (2400 parts); the sodium salt forms grey leaflets.



The following compounds are also described: 3'-sulpho-4'-amino-6-diphenylamino-1-naphthol-3-sulphonic acid; 3'-sulpho-4'-amino-7-diphenylamino-1-naphthol-3-sulphonic acid, from 7-amino-1-naphthol-3-sulphonic acid with benzidinesulphonic acid; 4'-amino-6-diphenylamino-1-naphthol-3-sulphonic acid, from benzidine with 1:7-dihydroxynaphthalene-3-sulphonic acid; and the compound, from 7-amino-1-naphthol-3-sulphonic acid with benzidinesulphonic acid and a mixture of ammonium and sodium hydrogen sulphites; the sodium salt forms glistening, grey leaflets. F. M. G. M.

Catalytic Decomposition of Phenylhydrazine by Cuprous Salts. ALEXANDER E. ARBUZOV and V. M. TICHVINSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 69—70).—When heated with cuprous chloride, bromide or iodide, phenylhydrazine undergoes catalytic decomposition according to the equation:

$$3\text{NHPh}\cdot\text{NH}_2 + \text{CuX} = 3\text{NH}_3\text{Ph} + \text{N}_2 + \text{NH}_3 + \text{CuX}$$

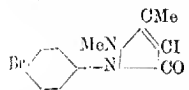
(compare Struthers, P., 1905, 95). In all cases, an unstable intermediate compound is formed, that given by the iodide having the composition  $\text{CuI}\cdot 2\text{NHPh}\cdot\text{NH}_2$ . Cuprous chloride is the most effective and the iodide the least so. T. H. P.

A Process for the Preparation of New Colouring Matters and its Application. BRONISLAW PAWLEWSKI (*Bull. Soc. ind. Mulhouse*, 1912, 82, 682—683).—When aniline in acid or alcoholic solution is oxidised at 50°–60° with ammonium persulphate, a black dye is obtained, which is considered to be bisimino-*p*-benzoquinone,  $\text{O}=\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ .

By changing the conditions, other brown or black anilinoquinones are formed. Similar colouring matters containing oxygen have been prepared from *m*-phenylenediamine, *o*-diamidine, and benzylaniline. They are easily fixed by cotton, linen or silk, with or without the aid of mordants. J. C. W.

Preparation of 1-*p*-Bromo-4 iodophenyl- and of 4-Bromo-1-*p*-iodophenyl 2:3-dimethyl-5-pyrazolone. FARBERGER VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254487).—The introduction of bromine and iodine into the molecule of 1-phenyl-2:3-dimethyl-5-pyrazolone confers on it a markedly increased therapeutic activity.

1-*p*-Bromo-4 iodophenyl-2:3-dimethyl-5-pyrazolone (annexed formula), colourless crystals, m. p. 163°, is obtained when a benzene solution of *p*-bromophenyl-2:3-dimethyl-5-pyrazolone (A., 1900, i, 695) is treated with finely powdered iodine and heated at 50–60° during two hours, whilst 4-bromo-1-*p*-iodophenyl-2:3-dimethyl-5-pyrazolone, pale yellow leaflets, m. p. 170°, is prepared by the bromination of 1-*p*-iodophenyl-2:3-dimethyl-5-pyrazolone (A., 1907, i, 84). F. M. G. M.

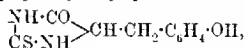


Hydantoins. XXI. Action of Ammonium and Potassium Thiocyanates on  $\alpha$ -Amino-acids. TREAT B. JOHNSON and BEN H. NICOLET (*Amer. Chem. J.*, 1913, 49, 197–204).—In an earlier paper (this vol., i, 293), it has been pointed out that ammonium and potassium thiocyanates behave somewhat differently towards  $\alpha$ -amino-acids. It has now been found that both salts combine with the acids to form the same thiohydantoins, but that the best yields are obtained by means of the ammonium salt.

When asparagine is treated with ammonium thiocyanate, 2-thio-3-acetylhydantoin-4-acetamide (Johnson and Guest, A., 1912, i, 807) is obtained in a yield amounting to 50% of the theoretical, whilst with the potassium salt a yield of only 6% is obtained.

Phenylalanine gives with ammonium thiocyanate a 94% yield of 2-thio-3-acetyl-4-benzylhydantoin, m. p. 176° (not 257° as stated by Johnson and O'Brien, A., 1912, i, 806); a somewhat smaller yield is obtained by the use of the potassium salt.

By the action of ammonium thiocyanate on tyrosine, a 94% yield is obtained of 2-thio-4-*p*-hydroxybenzylhydantoin,



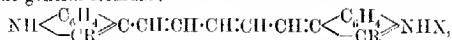
m. p. 211°, which forms pale yellow needles; if potassium thiocyanate is employed, only a very small yield is obtained.

2-Thio-3-benzylhydantoin (Johnson and Nicolet, A., 1912, i, 53) is obtained in 85–88% yield by the action of ammonium thiocyanate on hippuric acid, but in not more than 50% yield by the action of the potassium salt.

In the case of alanine, an excellent yield of 2-thio-3-acetyl-4-methylhydantoin (Johnson, A., 1912, i, 390) is obtained with ammonium thiocyanate, but only about 31% with the potassium salt.

The thiohydantoin of pyrrolidonecarboxylic acid (Johnson and Guest, A., 1912, i, 317) is readily obtained in good yield by means of ammonium thiocyanate, but only in small amount by the action of the potassium salt. E. G.

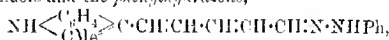
The Reactivity of the  $\beta$ -Unsubstituted Pyrrole Ring. III. Action of Cyanogen Bromide and Pyridine on Indoles. WALTHER KÖNIG and R. SCHRECKENBACH (*J. pr. Chem.*, 1913, [ii], 87, 241—257). —In view of the parallelism, previously shown to exist (A., 1911, 1, 808), in the reactivity of primary aromatic amines and phenols on the one hand, and of 3-unsubstituted indole derivatives on the other, the author has examined the behaviour of the latter compounds toward pyridine and cyanogen bromide, and finds that they yield dyes which have the general formula:



and are, therefore, closely related to the pyridine dyes derived from aromatic amines.

$\alpha$ -2-Methylindyl- $\epsilon$ -2-methylindolidene- $\Delta^{\gamma}$ -pentadiene hydrobromide,  $\text{NH} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \right\rangle \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{C} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \right\rangle \text{NHNBr}$ , is obtained in lustrous, golden leaflets by the action of hot acetone on its additive compound,  $\text{C}_{25}\text{H}_{21}\text{N}_3\text{Br} \cdot \text{C}_6\text{H}_5\text{N} \cdot \text{HBr}$ , with pyridine hydrobromide. The latter compound separates in green needles by the successive addition of pyridine and cyanogen bromide in ethereal solution to 2-methylindole, dissolved in methyl alcohol. The dihydrobromide, prepared by warming the monohydrobromide with acetone and hydrobromic acid, crystallises in lustrous, silky, bluish-green needles.

On treatment with aqueous sodium hydroxide and methyl alcohol, the hydrobromide yields the dye-base,  $\text{C}_{25}\text{H}_{20}\text{N}_2$ . This forms bluish-black needles, and is converted at  $220^\circ$  into a yellow substance, m. p.  $265^\circ$ , which probably has the same composition as the original dye-base, yields a phenylhydrazone (decomp.  $160$ — $170^\circ$ ), and when heated at 160 under diminished pressure decomposes, yielding 2-methylindole. The dye-base reacts with phenylhydrazine in alcoholic solution, yielding 2-methylindole and the phenylhydrazone,



which forms an amorphous, light yellow powder (decomp.  $170$ — $180^\circ$ ) containing alcohol (1 mol.).

On treatment with dry hydrogen chloride, the dye-base yields a hydrochloride,  $\text{C}_{25}\text{H}_{21}\text{N}_2\text{Cl}$ ; the perchlorate,  $\text{C}_{25}\text{H}_{20}\text{O}_4\text{N}_2\text{Cl}$ , forms small, compact, green crystals having a golden lustre, and crystallises with methyl alcohol in long, slender, bluish-green needles.

$\alpha$ -Indyl- $\epsilon$ -indolidene- $\Delta^{\gamma}$ -pentadiene hydrobromide,  $\text{C}_{25}\text{H}_{21}\text{N}_3\text{Br}$ , prepared from indole, cyanogen bromide, and pyridine in methyl alcohol solution, forms a microcrystalline, dark blue powder, containing pyridine (1 mol.).

$\alpha$ -2:4-Dimethylindyl- $\epsilon$ -2:4-dimethylindolidene- $\Delta^{\gamma}$ -pentadiene hydrobromide, prepared from 2:4-dimethylindole, yields on treatment with aqueous sodium hydroxide and methyl alcohol the dye-base,  $\text{C}_{27}\text{H}_{24}\text{N}_2$ , which forms microcrystalline, bluish-black needles; a dihydrobromide and a perchlorate, crystallising in green leaflets of a golden lustre, are also described.

The action of cyanogen bromide and pyridine on phloroglucinol and

resorcinol gives rise to blue pyridine dyes, which, however, are too unstable to be isolated. F. B.

[Preparation of 4-Chloro-5-bromoisatin.] KALLE & Co. (D.R.P. 254468).—4-Chloroisatin, a yellow, crystalline powder, m. p. 251°, is prepared by treating a cooled acetic-chromic acid solution of 4:4'-dichloroindigotin with concentrated nitric acid; when warmed with bromine (in acetic acid solution) it gives rise to 4-chloro-5-bromoisatin, red needles, m. p. 255°, which on treatment with phosphorus pentachloride furnishes 4-chloro-5-bromoisatin chloride, brown needles, m. p. 278°; the corresponding anilide was also prepared. F. M. G. M.

Preparation of 5:6:5':6'-Tetrachloroindigotin. FARBERWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.P. 251467).—4:5-Dichloro-2-nitrobenzaldehyde, yellow prisms, m. p. 73°, is prepared by the nitration of 4:5-dichlorobenzaldehyde; this when condensed with acetone in the presence of sodium hydrogen sulphite furnishes dichloronitrophenyl-lactyl ketone, m. p. 116°, which is readily converted by known methods into 5:6:5':6'-tetrachloroindigotin, a substance possessing valuable tinctorial properties. F. M. G. M.

Preparation of Dinitro-1:1'-dianthrimide. FARBERWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.P. 254186).—The nitration of dianthrimide (which has previously been described) takes place more smoothly and yields a definite characteristic product when carried out in the presence of boric acid.

1:1'-Dianthrimide (100 parts) and boric acid (65 parts) are dissolved in 1000 parts of concentrated sulphuric acid, treated at 5–10° with 27% nitric acid (122 parts), and left during two to three days at the ordinary temperature, when about 87% of the 4:4'-dinitro-1:1'-dianthrimide separates in glistening, coppery crystals. The m. p. is above 300°, and it is identical with the compound previously obtained by condensing 4-nitro-1-amino- with 4-chloro-1-amino-anthraquinone; on reduction it furnishes 4:4'-diamino-1:1'-dianthrimide. F. M. G. M.

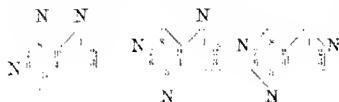
Preparation of *o*-Methylsulphites of Substituted Amino-arylpyrazolones. FARBERWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.P. 254711).—Compounds having valuable therapeutic properties are obtained when the substituted 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolones are heated with formaldehyde and sodium hydrogen sulphite; compounds obtained in this manner from the following pyrazolones have now been prepared. From 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone, sintering and decomposing at 231–233°; from 4-amino-1-*p*-tolyl-2:3-dimethyl-5-pyrazolone, sintering at 120°, decomposing at 125°; from 1-*p*-aminophenyl-2:3-dimethyl-5-pyrazolone, isolated as its hygroscopic, crystalline sodium salt; from 1-*p*-amino-phenyl-2:3:4-trimethyl-5-pyrazolone, also isolated as a crystalline



sodium salt; from 4-amino-1-*p*-ethoxyphenyl-2:3-dimethyl-5-pyrazolone, m. p. 113—115°, decomp. at 133—135°. The foregoing 4-amino-1-*p*-ethoxyphenyl-2:3-dimethyl-5-pyrazolone, m. p. 132—133°, is obtained by the reduction of 4-nitroso-*p*-ethoxy-2:3-dimethyl-5-pyrazolone.

F. M. G. M.

**Pyrimidines. LIX. Barbituryl- and 2-Thiobarbituryl-5-acetic Acids.** TRENT B. JOHNSON and EDWARD F. KOHMANN (*Am. Chem. J.*, 1913, 49, 184—197).—An account is given of experiments

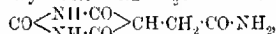


undertaken with a view to the preparation of compounds containing condensed pyrimidine and pyrrole nuclei, and corresponding with the indoles and pyrindoles (Perkin

and Robinson, T., 1912, 101, 1787). Compounds of this new class are termed 1:6:8-, 1:5:7-, and 2:5:7-pyrimazoles (annexed formulae).

A 1:6:8-pyrimazole has already been obtained by heating ethyl 6-chloro-2-ethylthiopyrimidine-5-acetate with alcoholic ammonia (A., 1911, i, 575); this compound, previously termed 2-ethylthiol-5:6- $\alpha$ -pyrrolidone-pyrimidine, is now designated 2-keto-7-ethylthiol-1:6:8-pyrimazole.

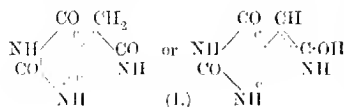
When ethyl ethane- $\alpha\beta$  tricarboxylate is treated with carbamide in the presence of sodium ethoxide, the sodium salt of barbituryl-5-acetamide is obtained, which crystallises with 4H<sub>2</sub>O. Barbituryl-5-acetamide,



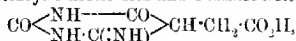
m. p. 258—261° (decomp.), crystallises in needles. Barbituryl-5-acetic acid,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained by the action of 20% hydrochloric acid on the sodium salt of the amide, separates in plates, becomes charred at 230°, and decomposes at 250°. An attempt to condense the amide to a 1:6:8-pyrimazole by the action of phosphoryl chloride on its sodium salt was not successful.

Thiobarbituryl-5-acetamide,  $\text{CS} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$ , prepared by the condensation of thiocarbamide with ethyl ethane- $\alpha\beta$ -tricarboxylate, crystallises in needles and decomposes at 272°; the sodium salt forms long, colourless prisms. Thiobarbituryl-5-acetic acid,  $\text{CS} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot 2\text{H}_2\text{O}$ , crystallises in needles and decomposes above 230°.

Ethyl cyanosuccinate condenses with carbamide with formation of a pyrimidine. The reaction does not take place smoothly, and only small yields of condensation products are obtained. In one experiment, barbituryl-5-acetic acid was pre-



produced, together with 2:5:7-*triketo*-1:6:8-*pyrimazole* (formula 1), which forms a brown powder and does not melt below 320°. In another experiment, barbituryl-5-acetic acid and 4-*iminobarbituryl*-5-acetic acid,



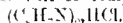
were isolated; the latter substance is a brown powder, and does not melt below 338°. E. G.

**Preparation of Azimino-[Triazole]-compounds in the Anthraquinone Series.** FARBENFABRIKEN VON FRIEDR. BAYER & CO. (D.R.P. 251715).—The azimino compounds having the general formula  $\text{A} \begin{array}{c} \text{NR} \\ \text{N} \end{array} \text{N}$ , where A is anthraquinone and R hydrogen, alkyl or aryl groups, and prepared by the action of nitrous acid on *o*-diaminoanthraquinones, are of technical value for the preparation of dyes. The preparation of the following compounds is described: From 1:2-diaminoanthraquinone, needles; from 2:3-diaminoanthraquinone, and from 1-*p*-tolylamino-2-amino-3-bromoanthraquinone, brown-yellow needles. The tinctorial properties of these compounds are enhanced by the introduction of halogens into the molecule.

F. M. G. M.

**Polymeric Indoles.** K. KELLER (*Ber.*, 1913, 46, 726—733).—The high-boiling residue obtained in the distillation of practically pure indole consists of a trimeride, *tri-indole*, which after recrystallisation from benzene can be obtained in colourless crystals, m. p. 167°. The polymerisation can be better effected by heating indole with an aqueous solution of metaphosphoric acid. When distilled in a vacuum, *tri-indole* decomposes completely into indole; it gives a *monocetyl* derivative, colourless crystals, m. p. 202°, and a *monobenzoyl* derivative, colourless, crystalline powder, m. p. 207°. These acyl compounds are remarkably resistant to alkalis. When benzoyltri-indole is heated in a vacuum, indole distils away, leaving a residue of *benzoyldi-indole*, colourless needles, m. p. 198°; this resisted all attempts at acetylation and hydrolysis. The easiest method for the preparation of benzoyltri-indole is by boiling together a benzene solution of indole with anhydrous sodium carbonate and benzoyl chloride, whilst a slow current of hydrogen chloride is passed through the mixture; the yield is then 90% of the indole taken.

The action of hydrogen chloride on a solution of indole in benzene yields a colourless salt of composition



presumably *di-indole hydrochloride*, but it was not found possible to isolate the corresponding base in a pure state.

From a consideration of the behaviour of the above tri-indole derivatives, the annexed structure is suggested for the base, the reactive indole nucleus being that on the left; this differs from the remaining two by being attached to the rest of the molecule at carbon atoms which are each adjacent to nitrogen atoms. D. F. T.



**Preparation of Formaldehyde Derivatives of Xanthine and its Substitution Products.** FARBENFABRIKEN VORM. FEINIG, BAYER & Co. (D.R.-P. 254488).—When xanthine, its derivatives, or the purine bases are gently heated in aqueous or hydrochloric acid solution with formaldehyde (or its generators), they furnish compounds of marked therapeutic value. The following are described: (1) From 1:3-dimethylxanthine and formaldehyde in aqueous solution, contains 14% formaldehyde, m. p. 265° when slowly heated, but if suddenly subjected to a temperature of 165—170°, violent decomposition occurs with regeneration of 1:3-dimethylxanthine.

(2) From 3:7-dimethylxanthine with paraformaldehyde in fuming hydrochloric acid solution, it forms characteristic needles, contains 14% formaldehyde, and does not melt below 300°.

(3) From xanthine and formaldehyde, contains 32% formaldehyde; and (4) from 3-methylxanthine contains 16% of formaldehyde. These compounds readily decompose in the organism with elimination of formaldehyde.

F. M. G. M.

**The Anomalies in the Solubility of Uric Acid (Colloidal Uric Acid).** HEINRICH SCHADE and E. LODEN (*Zeitsch. physiol. Chem.*, 1913, 83, 347—380).—If uric acid is suspended in boiling water, and alkali is then added very slowly until the mixture is just alkaline to phenolphthalein, the acid appears to pass into solution. This solution can be made by one of the following methods to set to a solid gel: (a) by the addition of concentrated sodium chloride solution; (b) by addition of other salt solutions, such as ammonium sulphate, which are ordinarily employed for the precipitation of colloids; (c) by addition of alcohol, and (d) by rapid cooling. The same phenomenon can be produced when the acid is neutralised by ammonia, lithium, sodium and potassium hydroxides, by the alkaline earths, and even ferric hydroxide. The appearance of the gel thus produced is described in great detail, and also the phenomena of its gradual transformation into the ordinary crystalline form. The colloid appears to be a super-saturated uric acid solution, in which the uric acid forms an adsorption compound with the alkali, which causes it to retain the colloidal form, and this adsorption compound appears to be a preliminary stage in the formation of the true chemical crystalline compound. The view here advanced can explain certain anomalies, to which Bechhold and Ziegler have called attention as regards the solubility of uric acid in serum.

S. B. S.

**Purines. VIII. 2:8 Dihydroxy-1:9-dimethylpurine and 2-Hydroxy-6:9-dimethylpurine.** CARL O. JOHNS (*J. Biol. Chem.*, 1913, 14, 1—7).—2:8 Dihydroxy-1:9-dimethylpurine is synthesised as follows: the potassium salt of 5-nitro-6-methylamino-2-hydroxy-pyrimidine (Johns, A., 1911, i, 506) when heated with methylhydrosulphide gives 5-nitro-6-methylamino-2-hydroxy-3-methylpyrimidine, the constitution of which is established by heating the methylated product with sulphuric acid, when 5-nitro-2:6-dihydroxy-3-methylpyrimidine (Behrend and Thurm, A., 1902, i, 833) is obtained.

On reducing the methylated product with freshly precipitated

ferous hydroxide, it is converted into 5-amino-6-methylamino-2-oxo-3-methylpyrimidine,  $\text{N} \begin{smallmatrix} \text{C}(\text{NHMe}) \cdot \text{C} \cdot \text{NH}_2 \\ \text{CO} \cdot \text{NMe} \cdot \text{CH} \end{smallmatrix}$ . This is very soluble and purified only with difficulty. The crude base was accordingly heated with carbamide and converted into 2:8-dioxo-1:9-dimethylpurine,  $\text{NMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NH} \begin{smallmatrix} \text{CO} \\ \text{CO} \cdot \text{N} \cdot \text{C} \cdot \text{NMe} \end{smallmatrix} \text{CO}$ .

By heating the potassium salt of acetyl-5:6-diamino-2-oxo-4-methylpyrimidine, 2-oxo-6:9-dimethylpurine,  $\text{N} \cdot \text{CMe} \cdot \text{C} \cdot \text{NH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot \text{C} \\ \text{CO} \cdot \text{NH} \cdot \text{C} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{CMe} \\ \text{CMe} \end{smallmatrix}$ , is obtained.

5-Nitro-6-methylamino-2-oxo-3-methylpyrimidine forms a bulky mass of hair-like crystals, m. p. 203°, to a colourless oil.

The picrate of 5-amino-6-methylamino-2-oxo-3-methylpyrimidine crystallises in long prisms, m. p. 200° (decomp.).

2:8-Dioxo-1:9-dimethylpurine crystallises in small, irregular plates, which do not melt or char at 320°.

2-Oxo-6:9-dimethylpurine separates in small prisms with square ends, which slowly turn brown at 315°; they give a murexide reaction.

E. F. A.

**Azomethines and Azo-dyes.** CAMILLE G. VERNET (*Arch. Sci. phys.*, *nat.*, 1913, [iv], 35, 148—172).—The azomethines derived from a number of diamines and benzaldehyde or its derivatives are described. In general they are formed quantitatively, the amount isolated depending on the manner in which the condensation is effected and the dilution of the solvents employed.

2-Mononitrobenzidine forms with benzaldehyde a yellowish-brown compound, m. p. 157°; with one molecule of *p*-nitrobenzaldehyde the product is red, m. p. 200—201°, with two molecules it is yellow, m. p. 205—206°; with dimethyl-*p*-aminobenzaldehyde it is yellow with an ill-defined melting point; with *o*-vanillin it is red, m. p. 206°.

*m*-Dinitrobenzidine and *o*-vanillin yield a reddish-brown product.

Benzidinesulphonate combines with one molecule of benzaldehyde to a yellow compound, m. p. 259—260°; with *p*-nitrobenzaldehyde to a brown compound, m. p. 302—304°; with dimethyl-*p*-aminobenzaldehyde the compound is yellow, m. p. 318°; with *o*-vanillin it is yellowish-red.

Diaminodiphenylamine and benzaldehyde form a yellow compound, m. p. 184—185°; with *p*-nitrobenzaldehyde the compound is black with a metallic lustre, m. p. 219°; with dimethyl-*p*-aminobenzaldehyde it is very similar, m. p. 222°; with *o*-vanillin it is brick-red, m. p. 207—208°.

3:3'-Diaminocarbazole and benzaldehyde yield a yellow substance, m. p. 186°; the product with *p*-nitrobenzaldehyde is red, m. p. 306—307°; with dimethyl-*p*-aminobenzaldehyde it is yellowish-brown, m. p. 256—268°; with *o*-vanillin it is brick-red, m. p. 254—255°.

*trans*-*o*-Diaminostilbene and benzaldehyde form a yellow product, m. p. 188°; with *p*-nitrobenzaldehyde it is orange-red, m. p. 228°; with

dimethyl-*p*-aminobenzaldehyde it is yellow, m. p. 227°, and with *o*-vanillin it is red, m. p. 228°.

*p*-Diaminostilbene yields a yellow compound with benzaldehyde, m. p. 254°; an orange-red compound with *p*-nitrobenzaldehyde, m. p. 242°; a reddish-yellow product with dimethyl-*p*-aminobenzaldehyde, m. p. 233°, and a red product with *o*-vanillin.

These azomethines are all very similar; the nitro-group has a greater effect in intensifying the colour than the substituted amino-group.

Most of the compounds have a normal composition with both amino groups condensed, but traces of the condensation products with a single molecule of aldehyde are formed at the same time.

A comparison is made of the colours obtained by soaking the material impregnated with sodium- $\beta$ -naphthoxide in the diazotised solutions of a number of diamines. Whereas benzidine gives a brown, thiobenzidine and benzidinesulphone give reddish-brown shades, mononitrobenzidine gives a red, *m*-dinitrobenzidine an orange, and the *o*-dinitro-derivative a garnet-red. With 2:2'- or 3:3'-diamino-carbazole the colour is almost black, and *p*-diaminostilbene gives a similar colour. The replacement of an atom of hydrogen by a univalent grouping has more influence on the colour than when two atoms of hydrogen are replaced by a bivalent substituent.

Each of the diamino-bases studied has been coupled with five acid compounds, namely, H-acid, chromotropic acid, Neville and Winther's acid, resorcinol, and naphthoic acid. The resulting compounds have not been analysed, but were directly utilised for dyeing tests. The colours obtained are detailed in tabular form; they act as substantive colours for cotton, and dye wool from acid solutions. E. F. A.

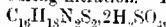
Thiophenols. III. *pp'*-Azophenyl Methyl- and *pp'*-Azophenyl Ethyl-sulphide. KURT BRAND and ADOLF WIRSING (*Ber.*, 1913, 46, 820—829).—The authors have extended their previous work on *pp*-azophenyl methyl sulphide (A., 1912, i, 666), and have investigated the corresponding ethyl derivative.

A concentrated aqueous solution of sodium hydroxide and sodium sulphide is gradually added to a boiling alcoholic solution of di-*p*-nitro diphenyl disulphide. From the cooled reaction mixture, the sodium derivative of *p*-nitrophenyl mercaptan,  $C_6H_4O_2NSNa \cdot 2H_2O$ , separates in golden leaflets, which decompose when heated slightly above 100°. The salt dissolves in water, forming a yellow solution, which, on addition of acid, becomes colourless and deposits *p*-nitrophenyl mercaptan. The solution absorbs oxygen with the formation of the disulphide. When warmed with an excess of ethyl bromide, the above sodium salt is transformed into *p*-nitrophenyl ethyl sulphide, m. p. 48° (Blankina, A., 1902, i, 282, gives 46°; L. Gattenmann, 41°). *pp'*-Azophenyl ethyl sulphide,  $ON_2(C_6H_4 \cdot SEt)_2$ , is obtained when a methyl-alcoholic solution of *p*-nitrophenyl ethyl sulphide is added to a boiling solution of sodium methoxide in methyl alcohol. It forms pale yellow needles, m. p. 27—28°. A sulphinium compound could not be obtained from it by the action of methyl sulphate.

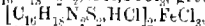
*pp'*-Hydrazophenyl ethyl sulphide, m. p. 76°, is obtained in the same manner as the corresponding methyl compound (*loc. cit.*). In alkaline alcoholic solution it is more readily oxidised by air than the

latter compound, and forms *pp'*-azophenyl ethyl sulphide, m. p. 132°. Treatment with concentrated hydrochloric acid transforms *pp'*-hydrazophenyl ethyl sulphide into *p*-aminophenyl ethyl sulphide hydrochloride, which readily gives up a portion of the hydrogen chloride. The free base, obtained from the hydrochloride by means of ammonia, has b. p. 165°/12 mm. (compare Auwers and Beger, A., 1894, i, 466; Monier-Williams, T., 1906, 89, 278; Gattermann, A., 1912, i, 986). *p*-Acetylaminophenyl ethyl sulphide, m. p. 116°, is obtained by shaking an aqueous solution of *p*-aminophenyl ethyl sulphide hydrochloride with sodium acetate and acetic anhydride, or by boiling the free base with the same reagents.

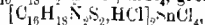
*pp'*-Azophenyl ethyl sulphide,  $N_2(C_6H_4SEt)_2$ , orange leaflets, m. p. 132°, is obtained by reduction of *p*-nitrophenyl ethyl sulphide by means of zinc and sodium hydroxide and oxidation of the hot, filtered solution by passing air through it. With mineral acids and strong organic acids it yields intensely blue solutions. The crystalline hydrochloride and trichloroacetate could not be obtained in the pure state, as they decompose during filtration. The sulphate,



green metallic needles, is obtained by the addition of sulphuric acid to a solution of *pp'*-azophenyl ethyl sulphide in glacial acetic acid. The following double salts have been obtained:  $C_{16}H_{18}N_2S_2 \cdot HCl$ ,  $HgCl_2$ , dark violet needles;  $C_{16}H_{18}N_2S_2 \cdot HCl \cdot FeCl_3$ , green leaflets;



dark green needles;  $C_{16}H_{18}N_2S_2 \cdot HCl \cdot SnCl_4$ , green leaflets;



dark green needles. They were prepared by mixing *pp'*-azophenyl ethyl sulphide with the metallic chloride in hot glacial acetic acid solution, addition of hydrochloric acid being necessary in the first, third, and fifth cases. They are immediately decomposed by water.

When *pp'*-azophenyl ethyl sulphide is heated with methyl sulphate and the reaction mixture treated with alcohol, light red crystals, m. p. 158°, are obtained. The aqueous solution yields, on addition of potassium iodide, a sulphinium iodide, m. p. 158–160°, analyses of which gives results from which the authors conclude that the substance is *pp'*-azophenyldimethylsulphinium iodide. The discrepancy between the m. p. now found and that previously given (174–175°, *loc. cit.*) is attributed to impurity of the specimen.

In extension of their previous work, the authors have prepared the double salt,  $(C_{16}H_{18}N_2S_2 \cdot HCl)_2 \cdot SnCl_4$ , green needles by the action of stannic chloride and hydrochloric acid on a solution of *pp'*-azophenyl methyl sulphide in glacial acetic acid. They also find that *pp'*-azophenyldimethylsulphinium methyl sulphate is more conveniently prepared by heating *p*-azophenyl methyl sulphide and methyl sulphate for an instant at the boiling point and treatment of the resulting product with alcohol. When this salt is treated with sodium hydroxide, it forms a new compound,  $C_{18}H_{16}O_8 \cdot N_2S_4$ , investigation of which is not yet completed.

II. W.

The Lakes of Hydroxylic Dyes. RICHARD MÖHLAU (*Ber.*, 1913, 46, 113–156).—[With JOHANNES MAETZEL.]—A brief account is first

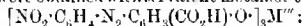
given of previous investigations of the compounds of dyes with mordants.

A number of compounds were prepared from various metallic mordants and hydroxylic dyes by precipitation. For the production of simple lakes derived from trivalent metals, solutions of a salt of the metal and of the potassium derivative of the dye were mixed. In order to obtain more complex lakes containing both trivalent and bivalent metals, the trivalent metal derivative was first prepared, and its solution in ammonium hydroxide was then treated with a solution of an equivalent amount of the salt of the bivalent metal (compare Livelti and Suida, A., 1884, 794; 1885, 315; Liebermann and Michaels, A., 1895, i, 108, 671; Biltz, A., 1906, ii, 78).

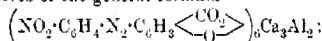
The fact that the lakes with the trivalent metals will dissolve readily in ammonium hydroxide indicates that the metallic atom is attached to hydroxylic oxygen, producing phenolic salts; the further introduction of the bivalent metallic atoms is then due to replacement of the hydrogen of the carboxyl or remaining hydroxyl group.

The following lakes of alizarin with trivalent metals were prepared, of the type  $\text{Me}'''(\text{C}_{14}\text{H}_7\text{O}_4)_3$ : *aluminium*, dark brown powder; *chromium*, yellow powder; *iron*, bluish-black powder. These could give calcium derivatives of the general formula  $\text{Me}_2'\text{Ca}_2(\text{C}_{14}\text{H}_6\text{O}_4)_6$ ; *aluminium calcium*, violet-brown; *chromium calcium*, deep violet; *iron calcium*, bluish-violet.

Of *p*-nitrobenzenesalicylic acid (the acid of alizarin-yellow-R), the following lakes were obtained with trivalent metals of the general formula



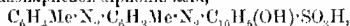
*aluminium*, red; *chromium*, brown; *iron*, chocolate. These gave calcium derivatives of the general formula



*aluminium calcium*, brownish-red; *chromium calcium*, brown; *iron calcium*, brownish-black.

The simple trivalent metallic lakes are more stable towards dilute acid and alkali than the more complex lakes containing two metals; of the latter, the aluminium calcium lakes are most stable and the iron calcium least, and those of alizarin are more stable than the corresponding derivatives of *p*-nitrobenzenesalicylic acid.

Benzenesazonaphtholsulphonic acid,  $\text{N}_2\text{Plr}\cdot\text{C}_{10}\text{H}_7(\text{OH})\cdot\text{SO}_3\text{H}$ , and azo-*o*-toluene-azonaphtholsulphonic acid,



give unstable *chromium* lakes, brownish-red and claret-red respectively, which are decomposed by dilute alkali or mineral acid; they are consequently regarded as being normal chromium salts and not phenolic derivatives. Complex lakes containing two metals could not be prepared from them.

D. F. T.

Preparation of Acetyl Derivatives of Aminoazobenzene, its Homologues and Analogues. KALLE & Co. (D.R.-P. 235884).—Acetyl derivatives of aminoazobenzene and of the aminoazo compound prepared from *o*-toluidine have been described previously; it is now

found that by prolonged heating with excess of the reagent, diacetyl derivatives are formed.

*Diacetylaminooctololuene* exists in two modifications, long, reddish-yellow needles, m. p.  $65^{\circ}$ , and in crystals, resembling potassium dichromate with m. p.  $75^{\circ}$ ; *diacetylaminooctobenzene* forms long, thin plates, m. p.  $103-104^{\circ}$ .  
F. M. G. M.

**Density and Solution Volume of Certain Proteins.** (Miss) HARRIETTE CHICK and CHARLES J. MARTIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 69-71).—From measurements of the density of casein, crystallised egg-albumin, crystallised serum-albumin and serum-globulin, and of the corresponding solution volumes in aqueous solution, it has been found that the density of the dissolved substance is in all cases greater than that of the free protein, the increase in density varying from 5 to  $8\frac{1}{2}\%$ . In the case of serum-albumin and serum-globulin, the solution volume of the protein is independent of the concentration, whereas the contraction, which attends the dissolution of casein, diminishes as the concentration increases. H. M. D.

**The Amount of L-Tyrosine in Proteins and the Accuracy of its Estimation.** EMIL ANDERHALDEN and DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1913, 83, 468-473).—The colorimetric method proposed for the estimation of L-tyrosine by Folin and Denis (A., 1912, ii, 1012) is shown to include other amino-acids, and to be untrustworthy. It is possible by crystallisation to separate completely the tyrosine from the products of protein hydrolysis, particularly when the necessary concentration of the liquids is effected under reduced pressure. Most of the published determinations of tyrosine in proteins have been made with insufficient care.  
E. F. A.

**Colloidal Solutions. I. Certain Metallic Peptonates.** EMANUELE PATERNO and FLORENTIN MEDIGRECEANU (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 65-68).—Solutions of iron, copper, zinc, and barium peptonate were subjected to prolonged dialysis, and after making up the volumes of the dialysed and residual solutions to the volume of the original solutions, measurements were made of the freezing point, total solids, ash, total nitrogen, and metal for each portion, the data being compared with the corresponding numbers for the original solutions. The observations seem to show that the substances formed by combination of peptone with the metal are, at any rate in the case of iron and copper, of colloidal nature.  
H. M. D.

**Porphyrinogen.** HANS FISCHER and ERICH BARTHOLOMAUS (*Ber.*, 1913, 46, 511-514).—By the action of a mixture of glacial acetic acid and hydrogen iodide in presence of phosphonium iodide on hamin in the cold, a colourless, crystalline reduction product,  $C_{33}H_{42}O_4N_4P$  of high molecular weight is obtained. This is termed porphyrinogen in view of its ready conversion into a red product having the spectroscopic properties of porphyrin.

Sodium methoxide acts on porphyrinogen forming phyllopyrrole;

VOL. CIV. i.

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also a porphyrin, of which the hydrochloride crystallises in centrically grouped needles—probably mesoporphyrin.

On oxidation, porphyrinogen yields methyl ethylmaleinimide and hæmætic acid.

The colourless porphyrinogen behaves as a sensibilising agent when injected into mice exposed to light rays. E. F. A.

**Pepsin.** II. SERAFINO DEZANI (*Atti R. Accad. Sci. Torino*, 1913, 48, 194—200. Compare A., 1910, i, 449).—The pepsin prepared according to the method previously described contains very little chlorine, and the author now finds that by suitable purification this element can be removed almost completely without diminishing the activity of the product. It appears, therefore, that the statements of previous authors that chlorine is a constituent of the substance are incorrect. R. V. S.

**Some Properties of Kojidiastase.** G. KITA (*J. Ind. Eng. Chem.*, 1913, 5, 220—222).—It has been generally assumed that koji (a culture of *Aspergillus oryzae* on steamed rice) contains two different saccharifying enzymes only, namely, amylase and glucase, and that the dextrose present in a liquid saccharified by means of koji is produced by these two enzymes. Comparative experiments on starch and maltose showed, however, that more dextrose was produced from the starch than from maltose, and the author concludes that koji contains a third enzyme which produces dextrose directly from starch without the aid of glucase.

Sodium chloride has a protecting action on koji-diastase when heated, but not on malt-diastase, whilst sodium phosphate, asparagine, and sulphuric acid impair its activity more quickly. The inhibitory action of the sodium chloride depends on the concentration of the diastase; in a dilute solution of the enzyme it is very marked, but not in a concentrated solution. The activity of koji-diastase may be conserved in brine solution for a long period. T. S. P.

**The Reversibility of the Ferment Action of Emulsin.** ÉMILE BOURQUELOT and J. COURRE (*Compt. rend.*, 1913, 156, 643—646; *J. Pharm. Chim.*, 1913, [vii], 7, 236—240. Compare A., 1912, i, 928; this vol., i, 212).—The state of equilibrium attained during the synthesis or hydrolysis of a glucoside in alcoholic solution under the influence of emulsin is independent of the amount of emulsin used and depends solely on the proportions of the components of the glucoside in the solution. The action is thus a true reversible reaction, the only effect of varying the concentration of the emulsin being to vary the rate at which equilibrium is reached. W. G.

**Hydrolysis of Amygdalin Under the Influence of Emulsin.** LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1913, 251, 85—89).—Kriebel's observation (A., 1912, i, 482) that certain kinds of emulsin react with amygdalin to give benzaldehydecyanohydrin is confirmed, and a series of experiments has been made to determine the mode of formation of the latter. It is shown that a portion of the benzaldehyde and

hydrogen cyanide which result from the gradual breaking down of amygdalin through mandelonitrile-glucoside and *d*-benzaldehyde-cyanohydrin re-combine to form *i*-benzaldehyde-cyanohydrin, and if an emulsin such as that from cherry kernels, which is very rich in *d*-oxynitrilase, is used, hydrolysis of the *d*-component of the inactive cyanohydrin ensues, *l*-benzaldehyde-cyanohydrin being left unaltered.

T. A. H.

**Distribution of Emulsin-like Enzymes.** LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1913, 251, 56–84).—The work done in recent years on "emulsin" shows that the latter may include different enzymes depending on its origin (A., 1910, i, 800; Armstrong and others, A., 1912, i, 816). The author has, therefore, investigated a large number of plants, particularly those which are known to be cyanogenic, with a view to ascertaining which of the ordinary components of "almond emulsin" they contain. For this purpose the mixture of enzymes prepared from the plant was mixed with (1) a solution of amygdalin, (2) a mixture of benzaldehyde and hydrocyanic acid (A., 1909, i, 74, 622), and (3) *dl*-benzaldehyde-cyanohydrin (Feist, A., 1909, i, 589), and the products of the reaction, if any, investigated. The results are described in detail in the original, and are also tabulated for convenience of reference. The following points of special interest are recorded. Enzymes capable of producing asymmetric synthesis or decomposition (reactions 2 and 3 above) are widespread in plants, although less so than those capable of decomposing amygdalin; this apparent difference may, however, be due to the fact that enzymes of the last-mentioned type are easier to detect by means of their product of reaction. Enzymes of these types may occur in plants which do not yield hydrogen cyanide, but in such cases they are not found in the leaves. These enzymes are not identical with those which decompose amygdalin, since in certain cases, such as *Hydnocarpus Wightiana* seeds, *Pongium edule* seeds, and *Prunus laurocerasus* leaves, negative results were obtained in reaction (1) and positive results with (2) and (3). Similarly, in other cases positive results were obtained for reaction (2) and negative results for reaction (3). An enzyme preparation from the seeds of *Taraktogenos Blumei* furnished in reaction (2) *l*-benzaldehyde-cyanohydrin instead of the *d*-isomeride furnished by enzymes derived from plants of the order *Prunaceae*; these seeds therefore appear to contain a *l*-oxynitrilase, which may also be present in the flowers of *Achillea millefolium*. No enzyme capable of producing optically active nitriles from ketones and hydrocyanic acid was observed. The enzyme of *Taraktogenos Blumei* is soluble in brine, but not in water.

T. A. H.

**Oxydases. VI. Tyrosinase is also a Deamidising Enzyme.** ROBERT CHODAT and K. SCHWEIZER (*Arch. Sci. phys. nat.*, 1913, 35, 140–147. Compare A., 1912, ii, 329, 611).—It has been shown previously that for the completion of the colour reaction between tyrosinase and *p*-cresol, the presence of an amino-acid is necessary. It is now proved that tyrosinase has a deamidising action on glycine, which it converts into carbon dioxide, ammonia, and formaldehyde.

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The change is greatly facilitated by the addition of limo water. The formation of formaldehyde is identified by means of Rimini's reagent (phenylhydrazine hydrochloride and potassium ferrocyanide), that of ammonia by means of Nessler's and Trilliat's reagents. The inter-action of *p*-cresol, glycine, and tyrosinase is prevented by the addition of calcium hydroxide; in its absence the blue coloration is obtained, and formaldehyde and ammonia are detected amongst the products of reaction.

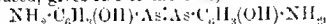
With alanine and tyrosinase, acetaldehyde is formed in place of formaldehyde. Benzaldehyde is obtained from phenylglycine and tyrosinase.

The presence of formaldehyde in plant tissues does not necessarily indicate photo-synthesis. Attention is drawn to the parallelism between the action of tyrosinase and of hydrogen peroxide on glycine (compare Dakin, A., 1906-1911). E. F. A.

**Preparation of Derivatives of Nitrohydroxy- and Amino-hydroxy-arylarsinic Acids Containing Sulphur.** FARNWERKE VORM. MEISTER, LUCIUS & BREXING (D.R.-P. 253757).—When an alkaline solution of 3-nitro-4-hydroxyphenylarsinic acid is saturated with hydrogen sulphide at the ordinary temperature, it gives rise to *nitrohydroxyphenylarsenosesisquisulphide*,  $[\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{As}]_2\text{S}_2$ , which crystallises from xylene in hard, yellow, nodular crystals, *m.* p. 160° (about).

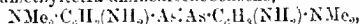
*Compounds* obtained by the action of sodium sulphide on 3-nitro-4-hydroxyphenylarsinic acid (a pale brown powder), of hydrogen sulphide on 3-amino-4-hydroxyphenylarsinic acid, and on its hydrochloride are also described. F. M. G. M.

**Aromatic Arsenic Compounds. IV. Preparation of 3-Nitro-4-dimethylaminophenylarsinic Acid and of 3-Nitro-4-hydroxyphenylarsinic Acid.** P. KARRER (*Ber.*, 1913, 46, 515-517).—*p*-Dimethylaminophenylarsinic acid is readily nitrated on solution in a mixture of acetic and nitric acids. When the mono-nitrodimethylaminophenylarsinic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NMe}_2) \cdot \text{As} \cdot \text{O}_3\text{H}_2$ , is warmed with sodium hydroxide, it is converted into 3-nitro-4-hydroxyphenylarsinic acid (Benda and Bertheim, A., 1911, i, 63), which in turn, when reduced, gives rise to the base,



corresponding with salvarsan.

When 3-nitro-4-dimethylaminophenylarsinic acid is similarly reduced, tetramethyltetra-aminoarsenobenzene,



is obtained. This compound has no curative action towards mice infected with trypanosomes.

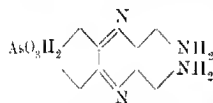
3-Nitro-4-dimethylaminophenylarsinic acid crystallises in lustrous, yellow needles.

The hydrochloride of tetramethyltetra-aminoarsenobenzene is a yellowish-white powder. E. F. A.

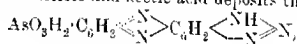
**Aromatic Arsenic Compounds. III. Triazoarylsinic Acids and Some of their Derivatives.** P. KARRER (*Ber.*, 1913, 46, 249-255).—Some triazophenylarsinic acids have been prepared

by the addition of sodium azoimide to the corresponding diazotised amines. They are very stable towards dilute sulphuric acid, and cannot be hydrolysed to aminophenols, but the *o*-nitrated azoimides give up nitrogen when heated and undergo rearrangement to *o*-dinitroso compounds (compare Zincke and Schwarz, A., 1899, i, 751), which can be readily condensed with dimethylaniline to phenazine derivatives.

*p*-Triazophenylarsinic acid,  $N_3 \cdot C_6H_4 \cdot AsO_3H_2$ , from *p*-aminophenylarsinic acid, crystallises in stout, white crystals, and gives a *monosodium* salt. 3-Iodo-4-triazophenylarsinic acid forms white crystals, and 3-nitro-4-triazophenylarsenic oxide,  $N_3 \cdot C_6H_3(NO_2) \cdot AsO$ , prepared from 3-nitro-4-aminophenylarsenic dichloride, which, in turn, is obtained from the arsinic acid, is a yellow, crystalline powder. 3-Nitro-4-triazophenylarsinic acid, a yellow, crystalline powder, loses nitrogen at  $75^\circ$ , and changes into 3:4-dinitrosophenylarsinic acid,  $C_6H_3(NO_2)_2 \cdot AsO_3H_2$ ; this condenses with dimethylaniline to form 2-(or 3-)dimethylaminophenazine-7-arsinic acid,  $C_{14}H_{12}O_3N_3As$ , as a blue dye which is very soluble in acetic acid and in sodium hydroxide. 2-Nitro-3-triazophenylarsinic acid also condenses with dimethylaniline, but 2-(or 3-)dimethylaminophenazine-8-arsinic acid is insoluble in sodium hydroxide and has a reddish tinge. 3-Nitro-4-triazophenylarsinic acid can also be condensed with *o*-phenylenediamine in glacial acetic acid, when the acetate of 2:3-diaminophenazine-7-arsinic acid separates as a brick-red powder. The free base (annexed formula) is yellow,



gives a *directyl* derivative as a yellowish-brown powder, and when treated with sodium nitrite and acetic acid deposits the compound,



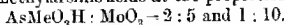
in the form of a brown powder.

J. C. W.

**Iso- and Hetero-poly-salts. VIII. Alkylarsinomolybdates.** ARNOLD ROSENHEIM and ROBERT BILECH (Ber., 1913, 46, 539—557. Compare A., 1911, i, 109, 265; ii, 116, 612; this vol., ii, 59).—In order to examine further the extension of Werner's co-ordination theory to poly-acids by Mioti and Pizzighelli (A., 1908, ii, 595), the authors have prepared a series of alkylarsinomolybdates. They find that the number of  $MoO_4$  or  $Mo_2O_7$  radicals which unite with the alkylarsinates to form complex compounds is intimately connected with the number of oxygen atoms in the arsinate anion, and diminishes as the number of alkyl radicals present increases. The basicity of the hetero-poly-acids so formed is either equal to, or, generally, higher than, that of the corresponding alkylarsinates. Normal hetero-poly-salts could not in all cases be obtained. This is attributed to the fact that the acids contain weakly electro-negative complex ions which are hydrolysed on neutralisation of the solutions. The composition of the hetero-poly-salts is found to depend on the electro-affinity of the central atom; more powerfully electronegative anions, such as the phenylarsinate- and *p*-hydroxyphenylarsinate-anions unite with  $MoO_4$

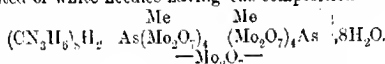
radicles, whilst the weaker electronegative anions, such as the dialkylarsinate-anion, unite with  $\text{Mo}_2\text{O}_7$  radicles.

The authors' experiments on solutions of cacodylic and molybdic acids agree with those of Miolati (*loc. cit.*). The latter, however, found breaks in the graph for the electrical conductivity of solutions of molybdic and methylarsinic acids at the proportions



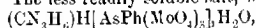
Since these figures did not agree with those obtained by the authors, the latter have plotted Miolati's graph on a larger scale, and find that it is not exact, somewhat weak breaks actually occurring at the proportions  $\text{AsMoO}_3\text{H} : \text{MoO}_3 = 1 : 6$  and  $1 : 9$ . The corrected result agrees with the authors' determinations.

A boiling aqueous solution of sodium methylarsinate was saturated with molybdic acid, and, after concentration, an excess of guanidinium chloride was added. Two *guanidinium* salts were thereby obtained, the less soluble of which was composed of rectangular plates having the formula  $(\text{CN}_3\text{H}_6)_2[\text{AsMe}(\text{Mo}_2\text{O}_7)_3] \cdot 11\text{H}_2\text{O}$ , whilst the more soluble salt consisted of white needles having the composition

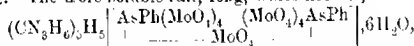


In alkaline solution only the latter salt was obtained.

Sodium phenylarsinate, when similarly treated, also yielded two *guanidinium* salts. The less readily soluble salt, white leaflets,



did not yield a neutral salt when boiled with excess of guanidinium carbonate. The more soluble salt, long, white needles,



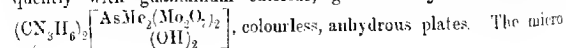
behaved according to conductivity measurements as the salt of a normal pentabasic substance. The hydrogen atoms could not be replaced by base in aqueous solution. In faintly alkaline solution, the more soluble salt was exclusively formed. When the latter salt was suspended in water and gently heated with guanidinium carbonate,

the salt,  $(\text{CN}_3\text{H}_6)_2\text{H}_2 \left[ \begin{array}{c} \text{AsPh}(\text{MoO}_4)_3 \\ \text{OH} \end{array} \right] \cdot 4\text{H}_2\text{O}$ , was obtained.

Precisely similar salts were obtained from those derivatives of phenylarsinic acid which did not form too powerfully electronegative anions; thus, from sodium *p*-aminophenylarsinate, the *guanidinium* salt,  $(\text{CN}_3\text{H}_6)_2 \left[ \begin{array}{c} \text{C}_6\text{H}_4\text{NH}_2 \\ \text{As}(\text{MoO}_4)_3 \end{array} \right] \cdot 5\text{H}_2\text{O}$ , pale yellow leaflets,

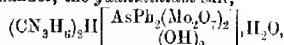
was prepared, whilst sodium *p*-hydroxyphenylarsinate yielded a *guanidinium* salt,  $(\text{CN}_3\text{H}_6)_2 \left[ \begin{array}{c} \text{C}_6\text{H}_4\text{OH} \\ \text{As}(\text{MoO}_4)_3 \end{array} \right] \cdot 2\text{H}_2\text{O}$ , white needles, and also a more soluble salt, crystallising in small plates. A complex salt derived from *p*-carboxyphenylarsinic acid could not be isolated.

Sodium cacodylate, when treated with molybdic acid and subsequently with guanidinium chloride, gave the *guanidinium* salt,



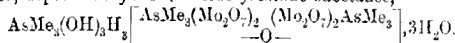
crystalline *lead*, *copper*, and *silver* salts were also prepared. The *potassium* salt, prepared from potassium cacodylate in the usual manner, formed microscopic needles of the formula  $K_2H \left[ \begin{array}{c} AsMe_3(Mo_2O_7)_2 \\ (OH)_2 \end{array} \right]$ . The corresponding *barium* salt was obtained by the action of barium chloride on the sodium salt.

In a similar manner, the *guanidinium* salt,

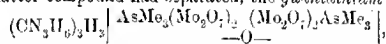


white, hexagonal plates, was obtained from sodium diphenylarsinate.

An aqueous solution of trimethylarsonium hydroxide was saturated with molybdic acid at its boiling point. The solution, when concentrated, deposited a yellow, microcrystalline substance,



When, however, guanidinium chloride was added to the above solution before the latter compound had separated, the *guanidinium* salt,

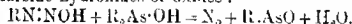


was obtained as microscopic, white plates.

When triphenylarsine oxide was dissolved in boiling aqueous sodium molybdate solution and the latter acidified by gradual addition of hydrochloric acid, a yellow, amorphous *substance*,  $\left[ \begin{array}{c} Ph_3 \\ As \\ Mo_2O_7 \end{array} \right]$ , was obtained.

H. W.

**Preparation of Organic Arseno-compounds.** HEINRICH BART (D.R.-P. 254345. Compare this vol., i, 115).—When solutions of *isodiaz*-compounds react with diarylarsenious oxides (or acids) they give rise to triarylarsine hydroxides or oxides:



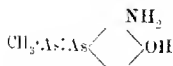
A 10% solution of sodium *p*-nitroisodiazobenzene is slowly treated with dinitrodiphenylarsenious acid and sodium hydroxide (1 mol.); on slowly heating to 75–80°, nitrogen is evolved, and on the addition of acid the trinitrotriphenylarsine oxide separates as a brown precipitate.

The required *dinitrodiphenylarsenious acid* is obtained by the careful reduction of dinitrodiphenylarsinic acid with hydrogen iodide in acetic acid solution; when heated it decomposes energetically without fusion.

F. M. G. M.

**Preparation of Unsymmetrical Arseno-compounds.** FARBERKE FORM. MEISTER, LUCIUS & BREXING (D.R.-P. 253326).—Unsymmetrical aromatic arseno-compounds have previously been prepared (this vol., i, 116), and this reaction has now been extended to the case of compounds containing both aliphatic and aromatic residues.

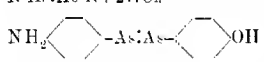
*3-Amino-4-hydroxybenzenearsenomethane* (annexed formula), a yellow powder soluble in dilute acids and alkaline hydroxides, is obtained when a methyl-alcoholic solution of 3-amino-4-hydroxyphenylarsenious oxide is treated with a similar solution of methyl arsenious oxide (A., 1906, i, 188), water added, and the mixture reduced with sodium hyposulphite.

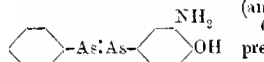


One or both of the arsenious oxides in the foregoing reaction can be replaced by the corresponding acids, in which case the reduction is carried out with stannous chloride and hydrogen iodide at  $-10$  to  $-20^{\circ}$ .

F. M. G. M.

**Preparation of Aromatic Arseno-compounds.** FARWELL, VERN. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254187. Compare A., 1909, i, 347; 1910, i, 148).—When aromatic arsenic acids are reduced in strongly acid solution they give rise to primary arsines of general formula  $R \cdot AsH_2$  ( $R = \text{aryl}$ ), which can be condensed with aryl. arsenious oxides or haloids to yield aromatic arseno derivatives (this vol., i, 117):  $R \cdot AsH_2 + R' \cdot AsO = R \cdot As \cdot As \cdot R + H_2O$ ;  $R \cdot AsH_2 + R' \cdot AsCl_2 = R \cdot As \cdot As \cdot R + 2HCl$ .

 4-Amino-4'-hydroxyarsenobenzene (annexed formula), a yellow powder, decomposes at about  $200^{\circ}$ ; 3-amino-4-hydroxy-4'-glycyloxyarsenobenzene (this vol., i, 116) darkens at  $120^{\circ}$  and decomposes violently at  $150^{\circ}$ , and 3-amino-4-hydroxyarsenobenzene (annexed formula) forms a yellow powder.

 Other compounds mentioned as being prepared by this method are 4:4'-diaminoarsenobenzene and 3:3'-diamino-4:4'-dihydroxyarsenobenzene.

F. M. G. M.

**Preparation of Aromatic Stibinic Acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 254421. Compare Trans., 1911, 99, 2286).—Phenylstibinic acid has previously been prepared (Hasenbäumner and others) by a somewhat complicated series of reactions; the following simple method is now described.

Antimony trioxide (140 parts) is dissolved at the ordinary temperature in 764 parts of hydrochloric acid (D 1.123), treated with sodium hydroxide (600 parts) in water (3000 parts), and rapidly cooled to  $0^{\circ}$ , when part of the sodium antimonite separates. A solution of aniline-diazonium sulphate (prepared from 93 parts of aniline and 147 parts of sulphuric acid) is then rapidly stirred in, either with or without the addition of copper paste; after some hours the mixture is carefully neutralised with sulphuric acid, filtered, and the phenylstibinic acid precipitated by the addition of hydrochloric acid. To purify the product from antimony trioxide it is dissolved in hot hydrochloric acid (D 1.123), and the solution saturated with solid ammonium chloride, when on cooling phenylstibinic oxychloride separates in glistening leaflets; this is isolated, decomposed with sodium carbonate, and the pure phenylstibinic acid precipitated with hydrochloric acid. As thus prepared, phenylstibinic acid is stable at  $250^{\circ}$  (Hasenbäumner gives decomp. point  $200^{\circ}$ ).

p-Hydroxyphenylstibinic acid and p-acetylaminophenylstibinic acid are similarly prepared from p-aminophenol and monoacetyl-p-phenylene diamine respectively; the sodium salt of the latter dissolves in water with a neutral reaction. p-Aminophenylstibinic acid, obtained by the hydrolysis of the foregoing acid, combines readily with aldehydes

(salicylaldehyde) to furnish hydroxybenzylidene derivatives or on diazotisation gives rise to a red azo derivative with alkaline  $\beta$ -naphthol.

F. M. G. M.

**Preparation of Nuclear Substituted Mercury Derivatives of Aromatic Hydroxy-acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.P. 255030).—The following therapeutically active organic derivatives of mercury have now been prepared.

*Mercurysalicylic acid*,  $\text{Hg}[\text{C}_6\text{H}_4(\text{OH})\cdot\text{CO}_2\text{H}]_2$ , a colourless powder, insoluble in water, is obtained by the reduction of *o*-hydroxymercurisalicylic anhydride with sodium formaldehyde-sulphenate, and is employed in the form of its neutral alkali salts.

*Mercury-bis-sulphosalicylic acid*, also employed in the form of its sodium salt, is similarly prepared from sodium mercurisulphosalicylate.

*Mercury-bis-arsenosalicylic acid*, a colourless powder, is obtained from mercury arsenosalicylic acid.

*Sodium mercuri-bis-2-naphthol-3 : 6-disulphonic acid* and *mercury-bis-1-hydroxy-m-tolyl-1-arsinic acid* are also employed in the form of their crystalline sodium salts.

F. M. G. M.

## Physiological Chemistry.

**The Influence of Phosphorus on Respiratory Metabolism.** OTTO HUNZ (*Zeitsch. Biol.*, 1913, 60, 187—310).—The respiratory exchange in rabbits sinks regularly during inanition. On the second day the nitrogenous output and the urea rise and remain at a constant level as the organ protein is utilised. In fat animals the consumption of the organ protein is delayed. In phosphorus poisoning the decrease in respiratory metabolism is not a specific effect of the poison on metabolism, but is secondary to pain and other symptoms produced. With small doses there is a slight increase in respiratory activity. The nephritis produced lessens the output of nitrogen, but in fat animals this is preceded by an increase. Carbohydrate metabolism is unaffected. The combustion of fat increases. No support is found for the hypothesis that the fat which appears in the organs ("fatty degeneration") is of protein origin. The permeability of the blood vessels is greatly increased.

W. D. H.

**The Coagulation of Blood.** WILHELM CHAMER and HAROLD PRINCE (*Quart. J. exp. Physiol.*, 1913, 6, 1—12).—If oxalate plasma is filtered through a Berkfeld filter, it does not clot when calcium chloride is added to it. This is due to removal of the platelets, which are still present in oxalate plasma prepared in other ways. The addition of calcium chloride to ordinary oxalate plasma liberates thrombokinase (Howell's thromboplastin) from the



platelets. Soluble calcium salts, in addition to this primary effect on the platelets, contribute also to the formation of fibrin under the influence of the substance liberated from the platelets. In paraffined tubes blood remains fluid because the platelets are intact; when transferred to glass tubes the platelets in contact with the glass disintegrate, and clotting ensues. The phenomena described by Nolf as "thromboplastic agencies" and "centres of coagulation" are due to the presence of platelets. Plasma free from platelets are not susceptible to the action of "thromboplastic agencies."

W. D. II.

**The Plasma of Propeptone.** HENRI STASSANO (*Compt. rend.*, 1913, 156, 735—738).—The plasma obtained after the intravenous injection of propeptone differs in several respects from plasma, to which salts have been added. The first is coagulated when diluted either with distilled water or even with a solution of an anti-coagulating salt, whilst the latter is only coagulated on dilution with water. The plasma of propeptone behaves thus as a mixture of serum and fibrinogen in decalcified solution. The coagulation of propeptone plasma on dilution is unaffected by change in temperature, whilst that of the saline plasma is checked by cooling. In tubes coated with paraffin wax, the former plasma coagulates on dilution with only a slight retardation, whilst the latter remains indefinitely liquid. The coagulating power of propeptone plasma towards the peritoneal serum from a horse is greater at the moment of dilution than two hours afterwards, whilst that of saline plasma steadily increases after dilution. These differences point to the fact that, whilst in the saline plasma the fibrin-ferment is in an inactive state, in the plasma of propeptone it is in the active state. W. G.

**The Transference of the Digestion Products of Proteins from the Mother to the Fœtus.** GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1913, 48, 362—372).—The distribution of nitrogen in the blood of the fœtus and mother in the case of dogs was determined both when digestion products had been injected into the jugular or femoral vein, and when either no injection had been made, or only saline had been administered. From the comparison of the various results obtained, the conclusion is drawn that protein digestion products can pass directly from the mother to the fœtus.

S. B. S.

**The Influence of Nutrition on the Amylase Content of Human Saliva.** C. LOVATT EVANS (*Biochem. Zeitsch.*, 1913, 48, 432—447).—The amylase content (estimated by determining the amount of maltose produced from a given starch solution in a given time by Bertrand's method) increases after a meal. The increase commences twenty to thirty minutes after a meal, and lasts for two to three hours, when it reaches a maximum and then wanes. The activity remains then small until the next meal is taken. The content is not affected after mock feeding (mastication of food without swallowing). A meal of purely protein content does not

increase the amylase. The mechanism of the secretion can be explained by assuming that carbohydrates act on the mucous membrane of the stomach and produce a hormone. The increase in amylase content is to be ascribed principally to the saliva produced by the parotid gland, which has about four times the enzymatic activity of that of the remainder of the glands. The parotid, furthermore, produces about half the total volume of the saliva.

S. B. S.

**The Behaviour of Plasteins in the Animal Body. I. The Relationships of Plasteins to Peptone Poisoning.** ERICH VON KSAATL-LENZ and ERNST P. PICK (*Arch. exp. Path. Pharm.*, 1913, **71**, 296).—If pepsin hydrochloric acid acts on a poisonous peptic digest, substances of higher molecular weight (plasteins) are formed which are not poisonous. The formation of plasteins in the body is regarded as protective. If the plasteins are again subjected to gastric action, poisonous products again arise; tryptic digestion is ineffective in this direction. The phenomenon is thus a reversible one. The final cleavage products of protein digestion are not poisonous. W. D. H.

**Pancreatic Digestion.** FRIEDRICH ABERGACH and HANS PICK (*Biochem. Zeitsch.*, 1913, **48**, 425—426).—Attention is called to the fact that, whereas natural pancreatic juice possesses the optimal hydroxyl ion concentration for lipoclastic or peptoclastic function, the digestion of proteins proceeds best in a medium more distinctly alkaline. This indicates that the preliminary digestion of proteins takes place for the most part in the stomach rather than in the intestine, the function of which is to digest the peptones. S. B. S.

**Comparative Physiology of Digestion. VI. Cellulose and Cellulose dissolving Enzymes in the Hepatopancreas of the Snail (*Helix pomatia*).** JERZY STANISLAW ALEXANDROWICZ (*Pflüger's Archiv*, 1913, **150**, 57—86).—Attention is directed to the two forms of crystalline cellulose, namely, those in plant sections, and the sphæro-crystals prepared *in vitro* by Gilson and Bütschli. The former have strong, doubly refracting properties; the sphæro-crystals are only feebly anisotropic. In plant membranes hemicelluloses are present, which increase their anisotropy. Crystallised cellulose is dissolved by the snail's hepatopancreas. Hence celluloses of different origin differ a good deal in solubility in the juice. It is suggested that the enzymes which dissolve cellulose and hemicellulose may be investigated microscopically in the study of the chemical composition of vegetable membranes. W. D. H.

**The Synthetic Powers of the Organism of the Dog.** KARL AUDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, **83**, 444—457).—The dog under observation was kept for three months on carbohydrate, fat, and the completely cleaved products of meat hydrolysis. It gained 10 kilograms in weight, and renewed its fur. Tryptophan and tyrosine are essential, and their absence is followed by untoward symptoms. Hopkins' view that tryptophan is essential for the formation of certain internal secretions is regarded as probable but unproven. W. D. H.

**Action of Ammonium Salts, Glucosamine and Gelatin on the Nitrogen Balance.** EMIL ABDERHALDEN and ARNO H. LAMPE (*Zeitsch. physiol. Chem.*, 1913, **83**, 409—424).—Experiments similar to those previously carried out on dogs are now recorded on two pigs. On most days there was a loss of nitrogen; in this and some other details the results differ from those of Grafe on pigs. A further series of experiments on a dog yielded much the same results. This dog died of tetanus, which is attributed to tetanus spores in the gelatin given. This is the first recorded instance of tetanus infection through the alimentary tract.

W. D. H.

**Utilisation of Calcium and Phosphoric Acid Compounds by the Animal Organism.** GUSTAV FINGERLING (*Landw. Versuchsstat.*, 1913, **79** 80, 847—870. Compare *ibid.*, **75**, 1).—Feeding experiments in which goats received, in addition to straw, blood, nuclein, starch, and oil, the following substances as sources of phosphorus: phytin, lecithin, casein, nuclein, nucleic acid, and disodium phosphate. The food was mixed with molasses to make it palatable.

The results showed that there is no essential difference in the utilisation of the different forms of phosphorus. The imperfect assimilation of the phosphoric acid of crude foods must, therefore, be due to other causes.

N. H. J. M.

**Comparative Investigations on the Content of Amino-acids in the Different Constituent Parts of the Nervous System. II. The Amino-acids of the Grey and White Substance of the Brain.** EMIL ABDERHALDEN and ARTHUR WEI (*Zeitsch. physiol. Chem.*, 1913, **83**, 425—440).—The results of the analyses of grey and white brain matter are given in tables, together with the methods used. The details relate to water, total nitrogen, ash, and various amino-acids.

W. D. H.

**The Action of the Diastatic Enzyme on the Glycogen within the Cells.** JULIUS GRODE and ERNST J. LESSER (*Zeitsch. Biol.*, 1913, **60**, 371—387).—The surviving liver and muscles of winter (glycogen-rich) frogs in oxygenated Ringer's solution lose little or none of their glycogen. The same was stated by Schiff in 1880. If the cells are destroyed mechanically, the glycogen disappears rapidly. The enzyme responsible for the change is considered to exist in the cells as a zymogen, which is converted into the active enzyme as the cells are killed.

W. D. H.

**The Behaviour of the Glycogen of the Frog in Anoxibiosis and Restitution. III.** ERNST J. LESSER (*Zeitsch. Biol.*, 1913, **60**, 388—398).—In the living summer frog (poor in glycogen) the anoxibiotic glycogen disappearance is about 50% in two hours at 20°. In restitution in the summer, contrary to what is seen in winter frogs, there is a well-marked new formation of glycogen. Under anoxibiotic conditions lasting two or three days, the

glycogen also is lowered by about 50%. Normal frog's blood contains no sugar when tested for by the method of Michaelis and Rona. In anoxymbiosis the blood contains 0.07% sugar, and minute amounts may pass into the urine.

W. D. H.

#### Comparative Anatomy and Physiology of the Pituitary Body.

PERRY T. HERRING (*Quart. J. exp. Physiol.*, 1913, 6, 73—108).—The pituitary bodies of the classes of vertebrates resemble one another in essential features. In elasmobranch fishes, however, the nervous lobe is absent.

No portion of the epithelial lobe in any case contained the active principles associated with the posterior lobe in mammalia. The *pars intermedia* by itself or the colloid matter separated from it have no specific effect on blood-pressure or kidney. The hormone which affects the mammary gland is obtainable from the skate's pituitary (which has no nervous lobe), and therefore appears to be a separate substance. It is still more abundant in the posterior (nervous) lobe in other animals; it is probable that it is a product of the epithelial lobe, and is stored in the *pars nervosa*. The latter is composed of modified ependyma and neuroglia cells permeated by a gelatinous substance containing fine granules and hyaline bodies. The granules are considered to be the representatives of the active principles of the nervous lobe; they are the products of the cells of the *pars intermedia* (in origin, a portion of the epithelial lobe); these are carried to, elaborated in, and stored by the *pars nervosa*.

W. D. H.

The Effects of the Administration of Extracts of the Pituitary Body and Corpus Luteum to Milch Cows. W. GAVIN (*Quart. J. exp. Physiol.*, 1913, 6, 13—16).—Under conditions of farm practice, no commercial benefit arises from the administration to dairy cows of these glandular extracts, whether given by the mouth, under the skin, or intravenously. Intravenous injection of pituitary extract causes more milk to collect in the lower parts of the udder, but no alteration in the total quantity per diem, or in the quality of the milk, occurs.

W. D. H.

The Effect of Pituitary and Corpus Luteum Extracts on the Human Mammary Glands. EDWARD A. SCHAFER (*Quart. J. exp. Physiol.*, 1913, 6, 17—20).—Observations on a woman of twenty-eight nursing her second child show that injection of pituitary extract intramuscularly, produced a tingling sensation in the breasts, and an increased flow of milk. The effect was not lasting, and a long time elapsed before there was again enough milk to feed the child. The effect of similar injections of extract of the corpus luteum was doubtful.

W. D. H.

The Liberation of Ions and the Oxygen Tension of Tissues during Activity. HERBERT E. ROAF (*Proc. Roy. Soc.*, 1913, B, 86, 217—218).—A preliminary account of an investigation of muscle by various kinds of electrodes, and the results give evidence that

hydrogen and probably chlorine ions are liberated during the act of contraction. There is also a fall in oxygen tension. W. D. H.

**The Summation of Muscular Contractions.** GEORGE R. MIXES (*J. Physiol.*, 1913, 46, 1—27).—Reasons are given for thinking that the liberation of acid in muscle as the result of excitation precedes the act of shortening and possibly causes it. When a second excitation can be produced before the first localised concentration of acid has had time to diffuse away, the result may be a summation of these localised concentrations, and so a greater effect on the contractile mechanism. Such an effect may, however, occur at a time when the general hydrogen ion concentration of the muscle is such that further increase tends only to diminish the power of the response of the muscle. W. D. H.

**The Energy Degraded in the Recovery Processes of Stimulated Muscles.** ARTHUR V. HILL (*J. Physiol.*, 1913, 46, 28—80).—A thermoelectric apparatus is described by which it is possible to estimate and record rapidly the rise of temperature of a muscle to within a millionth of a degree. The production of heat in a muscle excited in oxygen either by a single shock or a short tetanus continues for long periods after the mechanical response is over; but after the muscle has been kept in nitrogen for an hour there is no trace of heat production following the contraction; on being restored to oxygen this returns. Previous excitations or a prolonged tetanus, which diminish the oxygen tension in the muscle, lessen the heat production after the contraction. The "delayed heat" is due to usage of oxygen in the process of recovery; and recovery does not occur in the absence of oxygen. It is suggested that the contraction is due to liberation of lactic acid from some precursor; the acid increases the tension in some colloidal structure of the tissue; this precursor is rebuilt after contraction, oxygen is used, and heat is produced; when oxygen is absent, the heat produced is due to the breakdown of the lactic acid precursor. The oxygen appears to be used largely in oxidations whereby the molecular machine (like a steam engine charging an accumulator) builds up substances containing considerable amounts of free energy, which, as in the accumulator, can be discharged on subjecting the muscle to stimuli. W. D. H.

**The Extractives of Muscle.** III. TEMISTOCLE JONA (*Zeitsch. physiol. Chem.*, 1913, 83, 458—467).—Muscle extracts contain a fairly large percentage of gelatin, or rather of substances which behave like gelatin towards Schmidt's reagent. A dipeptide was also separated which, on analysis and determination of its constants, appears to be identical with the anhydride of *D*-alanine-*D*-alanine, which E. Fischer prepared by treating the ethyl ester of this dipeptide with ammoniacal alcohol. W. D. H.

**Products of Protein Cleavage which Produce Fatigue, and their Influence.** WOLFGANG WEICHARDT and ERWIN SCHWENK (*Zeitsch. physiol. Chem.*, 1913, 83, 381—402).—From the muscle

proteins, by means of electrolysis, certain high molecular products were obtained which cause, when injected into animals (mice), certain toxic symptoms, such as the signs of fatigue, slowing of the respiration, and depression of the body temperature. The effect of these *keno toxins*, as they are termed, can be counteracted by a number of substances of which the chemical composition is known, for instance, succinimide, glutarimide, phthalimide, piperidine, creatine, guanidine hydrochloride, and others. The same effect is produced by a group of substances of unknown composition which are spoken of as *retardins*; these can be extracted by acetone from digested protein. Further work on the relationships between activity and chemical composition is promised. W. D. H.

**Physiological Permeability of Cells. V. Narcosis of Lipoid-rich and Lipoid-poor Tissues of the Same Kind.** LOUIS CHOQUARD (*Zeitsch. Biol.*, 1913, 60, 101—162).—Heart muscle is richer in lipoids than skeletal muscle; the effect of narcotics on each was tried in order to determine the influence of lipoids. According to the Meyer-Overton doctrine, narcotics of the aliphatic series should produce narcosis in less concentration when applied to cardiac muscle as compared to skeletal muscle. But to this a number of noteworthy exceptions were found; ether, acetone, and acetylacetone produce narcosis in smaller concentrations in the lipoid-poor skeletal than in the lipoid-rich heart muscle. Acetal narcotises heart muscle, however, in much smaller concentrations than are necessary for skeletal muscle (which is in consonance with the lipoid hypothesis), but acetal narcotises skeletal muscle in higher concentrations than ether. The introduction of a halogen atom into the molecule leads to the result that the heart muscle is narcotised by a smaller concentration than skeletal muscle. The partition coefficient, solubility in fat solubility in water, does not account for this, for chloral hydrate, with the low coefficient of 0.23, narcotises heart muscle in the same concentration as ethyl bromide, which has a very high coefficient; probably the chemical influence of the halogenised material on the somewhat different biochemical structure of the two kinds of muscle is here being dealt with.

In the group of the univalent alcohols, the molecular weight increases as the lipoid solubility and the narcotic power in both tissues, but this relationship is not strictly parallel. For instance, the elevation of the partition coefficient of ethyl alcohol, as compared with propyl alcohol, is much greater than the rise in narcotic effect; the difference found was greater than stated by Overton.

Similar exceptional instances are found among the aldehydes. These experiments lead to the conclusion that the Meyer-Overton hypothesis is untenable. W. D. H.

**The Presence of Boron in the Animal Series.** GABRIEL BERNARD and HENRI ACHARD (*Compt. rend.*, 1913, 156, 732—735).

The authors have extended their work (compare A., 1912, ii, 854) on the presence of boron in animals, and have examined twenty-

seven other species from the different classes, finding boron in practically every case. They therefore consider that boron exists normally in very small proportions in the organism of all animals, being most abundant in the species of marine origin, whilst in others it is present only to the extent of 1 part in 100,000,000 of the living matter. W. G.

**The Composition of the Tissues with Respect to Non-volatile Fatty Acids and Cholesterol, and the Possible Existence of a "Lipocytic Constant."** ANDRÉ MAYER and GEORGES SCHAEFFER (*Compt. rend.*, 1913, 156, 487—491).—The authors have determined the amount of non-volatile fatty acids and cholesterol in the various organs of a number of normal animals, and find that, whilst the variation in content of the same organ for different animals of the same species is moderately wide, more particularly in the case of the fatty acids, yet certain points stand out clearly, namely, whilst these variations occur for a given organ of animals of the same species, the values group themselves in moderate limits round a mean value, but from one species to another very different values are obtained for the content with respect to these substances for the same organ, the values being greater for birds than mammals, and still greater for eels. The so-called "lipocytic constant," cholesterol/fatty acids, is characteristic for each organ, and independent of the species. W. G.

**The Action of Ultra-violet Rays on the Ear of the Rabbit.** VENCESLAS MOYCHO (*Compt. rend.*, 1913, 156, 577—579).—Exposure of the external surface of the ear to short irradiation (thirty seconds) produces no visible effect. If this is prolonged for one to twelve minutes, however, a series of phenomena appears. After two to five hours, local vaso-dilatation is noticeable, the portion which was exposed to the rays becoming red, this being accompanied by rise in temperature and tumefaction. The maximum effect is reached in twenty-four hours, then diminishes, and finally at the end of seven to twelve days the redness and high temperature completely disappear, and a persistent brown pigment appears. The irradiation appears to have a stimulating effect on the hair growth. The most active rays are those having  $\lambda$  3100–2500, and the cells acted on are situated at a depth of 1/10th to 1/6th mm. below the surface. W. G.

**The Influence of Heat on the Physico-chemical Behaviour of Human Milk, Cow's Milk, and Butter-Milk.** PAUL GROSSER (*Biochem. Zeitsch.*, 1913, 48, 427—432).—The milk was submitted to ultra-filtration in Bechhold's apparatus before and after boiling, and the amounts of calcium, nitrogen, and phosphorus in the filtrates were compared. It was found that after heating, the phosphorus and nitrogen in the filtrate of cow's milk was scarcely affected, whereas that of human milk was appreciably diminished.

In both kinds of milk the calcium in the filtrate diminished after heating.

S. B. S.

**The Therapeutic Action of Yeast on the Alimentary Multiple Polyneuritis of Guinea-pigs and Pigeons.** MAX BARSICKOW (*Biochem. Zeitsch.*, 1913, 48, 418—424).—The addition of various yeast preparations to the insufficient diet which produces the beri-beri-like symptoms in animals was investigated. In the case of guinea-pigs fed on oats and water, or on this diet with rice alone, the addition of yeast preparations exerted no beneficial effect. In the case of pigeons, however, fed on a similar diet, the beneficial effect of certain yeast preparations was marked. This effect was produced both by yeast of which the enzymes were destroyed by heat, by living yeast, and by permanent yeast preparations, but not by "cerolin," a preparation containing only the constituents of yeast soluble in organic solvents. It is suggested that the therapeutic action is due to nucleins or salts.

S. B. S.

**The Behaviour of Blood Sugar in Normal and Pathological Cases. VI. Blood-sugar Content in Cases of Anæmia, Liver, Intestinal and Other Diseases.** FR. ROLLY and FR. OPFERMANN (*Biochem. Zeitsch.*, 1913, 48, 471—479. Compare this vol., i, 307).—Severe anæmia, with its accompanying diseases, causes generally an increase in blood sugar, which is more or less normal in quantity in mild cases. In Greve's disease there is an increase only in severe cases. In Addison's disease the amount is either normal or sub-normal; in the latter case only when the disease is severe, and unaccompanied by infectious or toxic factors (tuberculosis, etc.). In scorbutic and eclamptic cases high values are generally found, which are due partly to the toxins. An increase was also found in cases of myasthenia and gangrene. In diseases of the liver and the alimentary tract there is an increase only when toxic factors are present (carcinoma, dyspnoea, abscesses, fever, etc.).

S. B. S.

**The Manganese Content of Transplanted Tumours.** FLORENTIN MEDIGRECEANU (*Proc. Roy. Soc.*, 1913, B, 86, 174—179).—The amount of manganese in transplanted mouse and rat tumours is small (0.004 to 0.012 mg. per 100 grams of fresh material), which is about the same as in the normal mammary gland of the mouse. No differences in the manganese of sarcoma and carcinoma were discoverable.

W. D. H.

**The Influence of Vapours of Technical Importance on the Organism. XXXII and XXXIII. Amyl Acetate and cyclohexanyl Acetate.** KARL B. LEHMANN (*Arch. Hygiene*, 1913, 78, 260—273).—Both the substances investigated have a relatively small toxicity, the cyclohexanyl acetate being about three times as toxic as amyl acetate, as measured by the amount necessary to produce narcosis. This greater toxic effect is, however, counterbalanced by the fact that it is considerably less volatile. Both substances can be safely employed in technical operations when the necessary precautions for ventilation, etc., are taken.

S. B. S.



**The Influence of Certain Cardiac Medicaments on the Electrocardium Curve.** ADOLF BICKEL and MICHAEL PASLOY (*Biochem. Zeitsch.*, 1913, 48, 459—470).—Certain digitalis and strophanthus preparations, and especially digistrophan, have the tendency to heighten certain points in the curve, whereas, in larger doses, the height of these points is diminished. In all cases there is a lengthening both of the heart phase and pause. Cardiotonin also causes a slowing of the heart action, increasing both the heart phase and pause. Valerian has no influence in this respect. The author discusses the therapeutic application of these various drugs, as deduced from their effects on the electrocardium curve. The experiments were carried out with dogs and rabbits. S. B. S.

**The Relationship between Heart Drugs and the Physiological Action of Cations.** ARTUR VON KONSCHIGO (*Arch. exp. Path. Pharm.*, 1913, 71, 251—260).—If a frog's heart is perfused with Ringer's solution free from calcium, the stoppage so produced can be counteracted by strophanthine; but if the solution is free from both potassium and calcium, strophanthine has not the power to resuscitate the heart. A heart poisoned with potassium again beats when strophanthine is applied. If a heart is stopped by a calcium-free solution, adrenaline and camphor cause weak contractions of the sinus, but caffeine has no effect. W. D. H.

**The Depressor Effect of Adrenaline on Arterial Pressure.** WALTER B. CANNON and HENRY LYMAN (*Amer. J. Physiol.*, 1913, 31, 376—398).—Stimulation of the cat's adrenal causes vaso-dilation and a fall of arterial pressure. Small doses of adrenaline have the same effect. After pithing, or extreme depression, the effect is pressor, but ergotoxine restores the depressor action. The effects are attributed to opposite actions of adrenaline according to the state of the muscle; relaxation occurs when the muscle is tonically shortened, and contraction when relaxed. W. D. H.

**Adrenaline and Glycemia.** HENRI BIERRY and (Mlle.) LUCIE FANDARD (*Compt. rend.*, 1913, 156, 480—482).—After injection of adrenaline to the extent of 0.001 gram per kilo. of body-weight, either intravenously or into the peritoneal cavity, there is marked progressive hyperglycemia and also a considerable rise in the combined sugar of the blood, which, however, increases more slowly than the free sugar. W. G.

**[Physiological] Action of Scopolamine.** MAX CLOETTA (*Arch. exp. Path. Pharm.*, 1913, 71, 290—292).—Polemical remarks on the controversy between Hug and Cushny (compare A., 1912, ii, 790; this vol., i, 226). W. D. H.

**The Action of Veratrine and Protoveratrine.** RUDOLF BOEHM (*Arch. exp. Path. Pharm.*, 1913, 71, 269—289).—The intensity of the action of protoveratrine on the frog's heart is much greater than that of veratrine; on nerve it is less active; on skeletal muscle

it is also less active, although its effects are substantially the same in kind. W. D. H.

**The Behaviour in the Organism of 2-Phenylquinoline-4-carboxylic Acid (Atophan).** W. SKÓRCZEWSKI and J. SOHN (*Bull. Acad. Sci. Cracov.*, 1912, 9, A, 885—887).—After administration of atophan, the urine gives the following reactions: (1) A yellow colour with concentrated hydrochloric acid. (2) A yellow precipitate with phosphotungstic acid. (3) A dark green colour with ammonium sulphate and ammonia. (4) A characteristic diazo-reaction with Ehrlich's reagent. These reactions are given neither by the drug itself nor by normal urine, but are due to an acid, which can be extracted from the concentrated urine by ether, and which after recrystallisation by ether and light petroleum has m. p. 231–232° after turning brown at 200°. Its formula,  $C_{18}H_{11}O_3N$ , corresponds with that of hydroxyphenylquinolinecarboxylic acid. The position of the hydroxyl group in this compound is not yet determined. S. B. S.

**Action of Arseno-aromatic Compounds ("606" and Neo-salvarsan) on the Hæmoglobin of the Blood.** R. DALMIER (*Compt. rend.*, 1913, 156, 629–631).—Salvarsan (diaminodihydroxyarsenobenzene) has no action on hæmoglobin either *in vitro* or *in vivo*. Neo-salvarsan (sodium diaminodihydroxyarsenobenzenemethylenesulphonate), on the other hand, produces marked hæmolysis and reduction of the oxyhæmoglobin when acting *in vitro*. On injection into the ear-vein of the rabbit, only a fugitive hæmolytic is noticeable, there being no reduction of the oxyhæmoglobin. W. C.

## Chemistry of Vegetable Physiology and Agriculture.

**Protein and Phosphorus Content of Azotobacter Cells.** CONRAD HOFFMANN (*Centr. Bakt. Par.*, 1913, ii, 36, 474–476. Compare Abstr., 1910, ii, 988).—During the course of earlier investigations the author found the protein content of *Azotobacter* cells to vary from 8.3–12.0%, and the phosphorus content to be 2.51–2.97%. These amounts vary considerably from those found by Stoklasa (*A.*, 1911, n, 429), and it is suggested that the differences are possibly due to differences in the methods employed in preparing the samples for analysis. The relatively high content (61.25–71.87%) found by Stoklasa might be attributed to removal of carbohydrates during washing, whereas the material used by the author was obtained, without washing, from agar cultures. If this were the case, the protein:phosphorus ratio ought to be the same in the two sets of results, but such agreement does not appear to exist. H. B. H.

**The Chemical Composition of Tubercle bacilli.** TADEUSZ KOZŃIEWSKI (*Bull. Acad. Sci. Cracow*, 1913, 10, A, 942—947).—When the bacteria are extracted with cold 96% alcohol, a small quantity of extract is obtained, which contains lipoids, colouring matter, and other substances. If the bacteria are extracted after alcohol treatment with hot acetone, relatively large quantities (20—24% of the dried bacteria) of a white, waxy substance are obtained, which is only slightly soluble on heating in most organic solvents, and is insoluble in mineral acids. On prolonged boiling with alcoholic potassium hydroxide, it yields a soap. Its formula agrees approximately with that of substance  $C_{42}H_{72}O_8$ , and the saponification number found was 125.2. The substance is probably an ester. When the bacteria are treated with 3—5% hydrochloric acid, a reducing sugar appears to pass into solution, which, even in concentrations of 2%, is optically inactive. The solution of sugar ferments with yeast. The author failed, in other experiments, to isolate glucosamine, from which he draws the conclusion that the bacteria do not contain chitin. S. B. S.

**Proteus vulgaris Considered as a Producer of Indole.** ALBERT BERTHELOT (*Compt. rend.*, 1913, 156, 641—643. Compare Herter and Broeck, A., 1911, ii, 758).—Numerous observers having obtained varying results as to the production of indole by different specimens of *Proteus vulgaris*, Hauser, the author has made a careful study of the question, and finds that, in the case of the fifty-seven specimens examined, all the *Proteus vulgaris* are capable of attacking tryptophan, giving either indole or indoleacetic acid, or more generally, a mixture of these two substances, and that there is no reason for distinguishing a species *Bacillus proteus anindoligenus*, as distinct from the *Proteus*-giving indole. The action of the microbe is variable not only with different specimens, but for the same race at different ages and under different conditions. W. G.

**Influence of Cæsium, Rubidium, and Lithium Salts on Yeast as Compared with Potassium and Ammonium.** THOMAS BOKORNY (*Biol. Zentr.*, 1913, 42, 141—142; from *Allgem. Brauer Hopfenz.*, 1912, 52, 1469).—Addition of rubidium and cesium sulphates to a nutritive solution containing sucrose (10), asparagine (0.1), peptone (0.025), monopotassium phosphate (0.1), and magnesium sulphate (0.025%) increased the yield of yeast, while lithium chloride and sulphate were injurious rather than beneficial. Potassium is essential; as much as 4.0% of monopotassium phosphate may be present without injurious effects. Ammonium salts up to 2% may be employed without injuring yeast. N. H. J. M.

**Biochemical Synthesis of Alkyl Glucosides (α Glucosides) by means of α-Glucosidase: α-Methyl Glucoside. Destruction of the α-Glucosidase in a Strongly Alcoholic Medium.** EMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, 156, 491—493; *J. Pharm. Chim.*, 1913, [vii], 7, 233—236).—The authors have synthesised α-methyl glucoside by the action of

$\alpha$ -glucosidase, obtained from bottom yeast (compare this vol., i, 323), on a solution of dextrose in dilute methyl alcohol. The glucoside is readily hydrolysed in aqueous solution by the enzyme. Both the synthesising and the hydrolysing influence of  $\alpha$ -glucosidase are destroyed by contact for forty-eight hours at 15–18° with 60% methyl alcohol. With 35% alcohol slow destruction also takes place. W. G.

#### Action of Boron Compounds on the Growth of Plants.

EMIL HASSELHOFF (*Landw. Versuchs-Stat.*, 1913, 79–80, 399–429. Compare Peligot, *Compt. rend.*, 1876, 83, 686; Morel, A., 1892, 651; Loew, *Flora*, 1892, 374; Hotter, A., 1890, 1338; Nakamura, *Bull. Coll. Agric. Tokyo*, 1903, 5, 509; Agulhon, A., 1910, ii, 236).—Small amounts of borax in water cultures (1 mg. per litre) acted favourably on the growth of plants, although the appearance of the plants indicated some injurious action. The same amount of boron in the form of borax diminished the yield. Both beans and maize are injured by 1.15 mg. per litre of boron.

In soil culture experiments, 0.125 mg. of boron (as borax) per kilo. of soil was not injurious to beans, whilst the same amount as boric acid is toxic. In some cases very small amounts (less than 0.1 per million of soil) seemed to have a stimulating effect.

The boron taken up by plants is deposited in the straw, and not in the seed. Although the production of spots on the leaves, under the influence of boron, seems to be the same in all kinds of plants, the effect on growth seems to vary with different plants.

N. H. J. M.

**The Value of the Chlorophyll Coefficients and their Relation to the Real Respiratory Coefficients.** LÉON MAQUENNE and EM. DEMOUSSY (*Compt. rend.*, 1913, 156, 506–512).—The authors have determined the respiratory quotient and the chlorophyll coefficient of some thirty-two species of plants, and as a result of this and previous work (compare A., 1912, ii, 1201) put forward a number of conclusions as to the conditions governing respiration and assimilation in the plant. In the case of green plants the normal respiratory quotient is generally greater than one during the total period of growth, but diminishes as the leaves grow older, its excessive diminution being a sign of decay or damage of the organs under observation. Leaves, with a respiratory quotient greater than one, increase the pressure of the air in which they breathe and vice versa. Certain species, particularly those rich in organic acids, are sensitive to prior conditions of light and temperature, exposure to strong light tending to diminish the respiratory quotient, but there is a particular state of equilibrium for each of such conditions, and to this, by adaptation, the plant tends to come. For a plant in equilibrium with external conditions there exists a simple relation between its apparent and real respiratory quotients and the composition of the medium in which it breathes and its coefficient of absorption for carbon dioxide, the cellular juice in a leaf sheltered from light being supersaturated with respect to the latter. The apparent chlorophyll coefficient is generally intermedi-

ate between the respiratory quotient and unity, the real coefficient being very near to unity. Changes in the ratio hydrogen : oxygen in the composition of the vegetable tissues are due mainly, if not entirely, to respiration, and but little to assimilation. The variations of the real respiratory quotient, due to changes in temperature, arise from changes in the chemical composition of the vegetable tissues under the given conditions, the chlorophyll coefficient being unaffected.

W. G.

**Absorption of Oxygen by the Respiratory Chromogens of Plants.** VLADIMIR I. PALLADIN and Z. N. TOLSTAJA (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 93--108\*).—Experiments with etiolated stems of *Vicia faba* and with zymin give the following results.

The protoplasm in which the respiratory chromogens effect absorption of oxygen possesses an alkaline reaction. These chromogens may be extracted from plants by means of methyl alcohol, and, in alkaline solution, are found to absorb oxygen eagerly from the air, with formation of a cinnamon-red pigment; peroxydases or hydrogen peroxide likewise cause oxidation of the chromogens. Aqueous extracts of plants also contain chromogens able to fix atmospheric oxygen, the power to do this being weakened or completely annulled by boiling the extracts.

Chromogens extracted by means of methyl alcohol undergo scarcely any oxidation in the air, but those obtained from plants subjected for some days to autolysis in an oxygen-free medium rapidly absorb oxygen from the air with development of pigments; the addition of hydrogen peroxide prevents the formation of pigment, the liquid remaining colourless. The chromogen modified by autolysis is hence termed "reducing." Autolysis with yeast converts ordinary chromogen into the reducing modification.

Plants which, after autolysis in absence of oxygen, give a chromogen rapidly blackening in the air, give no trace of pigment when the autolysis proceeds in presence of oxygen.

The respiratory chromogen from beans is probably catechol or some derivative of it.

Alcoholic fermentation is accompanied by the formation of a substance, which readily removes hydrogen from the respiratory chromogen, and oxidises it, by means of atmospheric oxygen, to water; this withdrawal of hydrogen from the chromogen is not prevented by boiling the products of fermentation.

Thus, the respiratory chromogen,  $R \cdot H_2$ , like leuco-compounds, gives up its hydrogen to the absorbed oxygen with formation of pigment,  $R$ , and water.

Palladin's previous statement that, during respiration of plants the carbon is oxidised, not by the oxygen of the air, but by water, is completely confirmed by the results of Wieland's investigations (*A.*, 1912, i, 348, 944), which showed that the oxidation of aldehydes (intermediate products of alcoholic fermentation) may proceed by removal of oxygen from water with preliminary formation of hydrates. The removal of the hydrogen formed by the decomposi-

\* and *Biochem. Zritsch.*, 1913, 49, 381--397.

tion of the water, which in Wieland's experiments was effected by means of methylene-blue or quinonoid compounds, is brought about in the case of plants by the respiratory chromogens; according to Bach, the decomposition of the water is a result of the action of reductases.

It is quite probable that, in the oxidation of chromogen to pigment, water is not immediately formed, but that the first product is either hydrogen peroxide (compare Manchot, A., 1901, i. 565, 574; ii. 93) or an organic peroxide (Bach's oxygenase).

T. H. P.

**The Migration of Mineral Constituents and the Displacement of These Constituents in Leaves Immersed in Water.** GUSTAVE ANDRÉ (*Compt. rend.*, 1913, 156, 564-566).—The author has estimated the mineral constituents in the dry matter of chestnut leaves plucked at various times during the summer of 1912. The figures, whilst varying in the same direction, differ considerably from the results obtained for 1911 (compare this vol., i. 233). The total nitrogen and phosphorus diminish with increase in age of the leaf, whilst the sulphur, calcium, magnesium, and potassium increase as the leaf grows older, the increase in sulphur and calcium being probably largely due to the accumulation of calcium sulphate in the leaf.

The figures for the percentage loss of mineral matter during immersion in water for one month are of the same order as those obtained for leaves grown in 1911 (*loc. cit.*), calcium being the most resistant to exosmosis.

W. G.

**The Germination of Seeds which have been Chemically Treated and Exposed to Light.** FRIEDRICH SIMON (*Biochem. Zeitsch.*, 1913, 48, 410-417).—Seeds of various plants (cress, oats, radishes) were allowed to germinate after treatment with ferric and uranyl sulphates, both when kept in the dark after the action of the reagent, and when exposed to sunlight. The percentage of the number of plants which germinated after five days was determined and compared with the number of seedlings obtained from seeds which had not been chemically treated, some of which had been exposed to light, and others kept in the dark. The results are tabulated, and it was found that in some cases (but by no means all) the seeds which had been exposed to light germinated more than those which had been kept in the dark. The action of the light and chemicals differed, however, in the different varieties of seed.

S. B. S.

**Alleged Constant Occurrence of Iodine in Cells.** JOHANNA BABY (*Ber. deut. bot. Ges.*, 1913, 31, 35-47).—The examination of numerous plants for iodine gave negative results invariably. Further experiments were made to ascertain whether plants absorb iodine from solutions containing potassium iodide. The results were negative.

The conclusion drawn by Justus (A., 1902, ii. 311) that iodine

is always present in the cell nucleus, animal and vegetable, is therefore incorrect.

N. H. J. M.

**Formation of Carbamide by Higher Plants.** ROBERT FOSSE (*Compt. rend.*, 1913, 156, 567—568. Compare A., 1912, ii, 1203).—Carbamide has been found in wheat, barley, maize, peas, clover, and beans, germinated under conditions excluding the presence of carbamide in the medium. Its presence has been proved in the seed during germination, but with the seed in a state of repose a negative result was obtained in the case of the white lupin and the bean, and a positive result with wheat, maize, and peas. In the case of the bean, after six weeks' germination no carbamide could be detected in the cotyledon, but it was found in the plumule to the extent of 0.112 gram per kilo. of fresh material. It was also present in the embryo of the haricot. Finally, its presence has been proved in the plumule of maize, aseptically germinated, and in the adult plant developed on a sterile, nutritive liquid according to Mazé's method.

W. G.

**Presence of Callose in the Membrane of the Marine Siphonaceous Algæ [Siphonates].** ROBERT MIRANDE (*Compt. rend.*, 1913, 156, 475—477).—The membrane of the *Caulerpa* contains no true cellulose, but is composed of two substances, one belonging to the group of pectins and the other to the calloses. This holds good for all the *Siphonates* with the exception of the *Laucheriaform*, which possess a celluloso-pectic membrane. The *Siphonates* thus form a distinct group, not only by reason of their anatomic characteristics, but by the chemical constitution of their membrane.

W. G.

**Influence of Temperature on the Development of Active Principles in Some Medicinal Plants.** JAMES BURMANN (*Bull. Soc. chim.*, 1913, [iv], 13, 246—248. Compare A., 1912, ii, 379).—By a comparison of the quantities of active principles present in colchicum, digitalis (*D. umbigra* and *D. purpurea*), aconite, and belladonna plants gathered under the same conditions each year from 1907—11 with the mean temperature prevalent during each year, the author is led to the conclusion that the alkaloidal or glucosidic content of a plant is a function of the mean temperature of the year during which it was grown.

H. W.

**Production of Oxalic Acid by *Aspergillus niger*.** CARL WEHMER (*Centr. Bakt. Par.*, 1913, ii, 37, 31—33).—Polemical against Buromski (this vol., i, 230), with special reference to the methods used for the estimation of oxalic acid in cultures.

H. B. H.

**Calotropis procera. A New Digitalis-like Drug.** LOUIS LEWIN (*Arch. exp. Path. Pharm.*, 1913, 71, 142—156).—A full botanical account is given of the plant, one of the *Asclepiadaceæ*. The active principle is called calotropin, but it has not yet been prepared pure for chemical analysis. The main fact is expressed in the title, namely, that it belongs to the drugs which act on the heart like digitalis.

W. D. H.

**Enzyme Action. IV. Occurrence of a Urease in Castor Beans.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, 35, 292—294. Compare Falk and Nelson, A., 1912, i, 523, 593; Falk and Hamlin, this vol., i, 303).—In continuation of a study of the enzymes of the castor bean, the presence of a urease has been demonstrated, which is rendered inactive by heat. E. G.

**Constituents of the Seeds of *Croton tiglium*.** ERNST WINTERSTEIN and M. A. JECOROV (*Landw. Versuchs-Stat.*, 1913, 79—80, 535—539).—The seeds examined contained 5–10% of nitrogen as proteins, and 0.19 and 0.19% of nitrogen as bases and amino-acids respectively. The proteins yield the usual cleavage products. When the seeds, freed from fat, are kept for sixteen days at 37–40° in presence of toluene, chloroform, and some sodium fluoride, xanthine bases, arginine and lysine are produced. The solution from the lead acetate precipitate contained the following amounts of nitrogen: as bases, 1.437; as ammonia, 0.3514; and as amino-acids, 1.7648 grams (from 500 grams of seeds). N. H. J. M.

**The Acids of Fungi.** E. HERRMANN (*Chem. Zeit.*, 1913, 37, 206).—Oxalic, fumaric, and malic acids are widely distributed in fungi, and usually occur as calcium salts. Oxalic acid, supposed to be derived by oxidation of carbohydrate, is the commonest. Malic acid is sometimes found as potassium salt. Fatty acids also occur in fungi, particularly palmitic acid. Formic, acetic, and butyric acids are characteristic of individual species. Ergotic and sclerotic acids are characteristic of ergot. Telephoric acid, present in the cuticle of some fungi, is a pigment. E. F. A.

**Composition of Some Fungi, and the Products of Their Autolysis.** ERNST WINTERSTEIN, C. REUTER, and R. KOROLEV (*Landw. Versuchs-Stat.*, 1913, 79—80, 541—562).—The fat of *Boletus edulis* contains 0.52% of a cholesterol, m. p. 160°;  $[\alpha]_D^{20}$  –133° in 5% chloroform solution. The following substances were obtained from the fungus: inactive alanine, valine, phenylalanine, small amounts of amino-acids and trimethylamine, guanine, adenine, hypoxanthine, trimethylhistidine, and tetramethylenediamine.

In the autolysis of *Boletus*, 80–90% of the total dry matter becomes soluble; the insoluble portion contains little nitrogen. The solution contained small amounts of guanine, some hypoxanthine, but no adenine or histidine. Trimethylhistidine, much tetramethylenediamine and isoamylamine, and a great deal of ammonia were found.

*Agaricus campestris*, *Cantharellus cibarius*, and *Craterellus cornucopioides* were also subjected to autolysis.

The results show that the proteins of fungi are to a great extent decomposed into their simple crystalline cleavage products, and probably peptones and polypeptides as well. It is probable that autolytic processes occur in the symbiosis of root nodules (compare Shibata, *Jahrb. wiss. Bot.*, 37, 643). N. H. J. M.



The Presence of Gentiopiricin, Gentianose, and Sucrose in the Fresh Roots of *Gentiana punctata*. MARC BRIDEL (*Compt. rend.*, 1913, 156, 627—629; *J. Pharm. Chim.*, 1913, [vi], 7, 289—292. Compare this vol., i, 149).—The author has isolated in a pure, crystalline state, and characterised, gentiopiricin, gentianose, and sucrose from the fresh roots of *Gentiana punctata*, and has also obtained evidence of the presence of a supposed new sugar. W. G.

Formation of Acetaldehyde during the Anaërobie Respiration of Poplar Blossom. S. KOSTYTSHEV, ELISE IL'Y. BENET, and A. SCHELOUMOV (*Zeitsch. physiol. Chem.*, 1913, 83, 105—111. Compare Palladin and Kostytshev, A., 1906, ii, 696).—Considerable quantities of freshly gathered poplar blossoms were kept in a stream of hydrogen, and the carbon dioxide, alcohol, and other volatile products formed were measured. The ratio of  $\text{CO}_2$ : $\text{C}_2\text{H}_5\text{O}$  during respiration varied from 100:35 to 100:55, and differed from that obtained in alcoholic fermentation. In addition, acetaldehyde is formed. The amount of sugar in the fresh flowers is not large, and it is almost entirely used up during the experiment. The excess of carbon dioxide formed over that produced during alcoholic fermentation is attributed to the decomposition of other substances. The formation of acetaldehyde is considered to be due to the oxidation of active hydrogen attached to reductase and consequent partial retardation of the reduction of acetaldehyde to alcohol (compare this vol., i, 323). E. P. A.

A New Rhubarb from Altai. ALEXANDER TSCHURCH and M. RUSZKOVSKI (*Arch. Pharm.*, 1913, 251, 121—136. Compare A., 1905, ii, 851; 1907, ii, 501; and Tutin and Clewer, T., 1911, 99, 946).—A proximate analysis of roots from an unidentified species of rhubarb collected at Altai shows that it belongs to the "rhaponticum" group. The constituents observed are rhaponticin, chrysophanol, emodin methyl ether, emodin, dextrose, tannoglucosides, and anthraglucosides; the last two groups of substances yield respectively rheum-red and rheonigrin on hydrolysis by acids. Rhein is absent. T. A. H.

The Oil Seed of *Ximenia Americana*, L. F. SCHRODER (*Arch. Kais. Gesund.*, 1912, 43, 454—474).—An account of the constituents is given. The seeds consist of 32.3% shell, and 67.6% kernel; the latter contains 2.99% moisture, 66.0% fat, 15.2% proteins, 3.0% crude fibre, 2.19% ash, and 10.46% nitrogen free extract. No saponin, alkaloid, or cyanogenetic glucoside was found. The kernels also contain about 1% of a caoutchouc-like substance, which yields a tetrabromide. The oil varies a little in physical properties depending on the method of preparation; it is yellow, semi-solid, possesses a sharp after-taste, and has the following constants:  $D_{15}^{20}$  0.9205 to 0.9220; saponification number, 173.2 to 177.0; iodine number, 80.3 to 85.05; Hehner number, 93.9 to 94.8; Reichert Meissl number, 1.61 to 2.45; Polenske number, 0.12 to 0.21; unsaponifiable matter, 0.46 to 0.55%. The viscosity in Engler degrees varied from 19.2 to 37.1 at 25°, and from 6.6 to 11.3 at 50°, the

highest value in each case being for oil extracted by ether, and the lowest for oil extracted by acetone. The total fatty acids included 75% of liquid fatty acids, and 10% of arachidic acid.

The shell contained 1.07% moisture, 5.9% fat, 9.05% proteins, 24.83% crude fibre, 12.78% ash, and 46.32% nitrogen-free extract.

T. A. H.

**Biochemistry of Sea Weeds.** HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1913, 83, 171—197).—Fucosan, the constituent of the bladders of the *Fucoidae* which is coloured red by vanillin and hydrochloric acid, has strong reducing properties; it is precipitated by lead acetate and in acid solution by gelatin solutions. Its solutions have an astringent taste resembling tannin. On oxidation, phycophæin is obtained. No sugar is eliminated on boiling fucosan with dilute sulphuric acid.

Mannitol has been found in several *Fucus* and *Laminaria* species. The sweet-tasting, white substance, which often covers the whole thallus of *Laminaria* on drying, is mannitol.

Dextrose or levulose were found in small quantity in four of the *Fucoidae* investigated, but in none of the *Florideae*. Several of the *Fucoidae* contain also a dextrin-like polysaccharide, laminarin, which is regarded as a reserve material built up from dextrose and corresponding with starch in the higher plants.

Two species, *Ascophyllum nodosum* and *Fucus vesiculosus*, which contain fat, contained very little laminarin.

The *Florideae* contain starch, which gives dextrose when boiled with dilute acids, and is quickly hydrolysed by malt diastase.

The seaweeds are rich in slimy cell-wall constituents. Algin and fucidin, obtained from the *Fucoidae*, are described briefly, as well as similar products from the *Florideae*.

E. F. A.

**Nutrition of Green Plants with Ammonium Salts.** EMBICO PASTANELLI and G. SEVERINI (*Bied. Zentr.*, 1913, 42, 98; from *Stuz. sper. agrar. ital.*, 1911, 44, 873).—Sand-culture experiments in which wheat and mustard were supplied with different ammonium salts under sterilised conditions. Sodium nitrate was also employed.

The greatest amounts of leaf were obtained with sodium nitrate, whilst ammonium salts produced the greatest amount of seed.

The only injurious effects were observed when ammonium chloride was employed, and in the case of mustard, with ammonium citrate. The best results with wheat were obtained with the organic ammonium salts, then the insoluble ammonium magnesium phosphate, and next with sodium nitrate. Mustard developed most quickly under the influence of sodium nitrate.

N. H. J. M.

**Changes of Phosphoric Acid in Plants at Different Periods of Growth and with Different Phosphorus Manures.** LEOPOLD SEIDLER (*Landw. Versuchs Stat.*, 1913, 79-80, 563-610). Pot experiments in which barley and oats were grown in different soils, without phosphorus and with superphosphate, bone meal, and basic slag respectively.

The result obtained by Staniszkis with millet, indicating that the nitrogen increases in the parts above ground to the end, was partly confirmed. In the roots, however, there is a diminution in the amount of nitrogen. The amount of phosphoric acid taken up is not always in proportion to the production of dry matter. Inorganic phosphates which, at first, are taken up in considerable amounts are, as vegetation proceeds, to a great extent converted into organic phosphorus compounds. In barley the organic phosphorus is chiefly in the forms of protein and lecithins, whilst in oats phytin frequently predominates. The phosphoric acid of phytin, which generally forms only a fraction of the total phosphoric acid, increases in the whole plant to the end of the vegetative period; in the roots it generally diminishes.

As regards the relation between the inorganic and organic phosphorus, the latter increases in barley, and generally in oats, as vegetation proceeds; in oats, however, the amount of organic phosphorus generally remains less than the inorganic phosphorus.

N. H. J. M.

**The Significance of the Lime-Magnesia Ratio in Soil Analyses.** P. L. GILE and C. N. ACETON (*J. Ind. Eng. Chem.*, 1913, 5, 33—35).—Loew has put forward the hypothesis that plants make their maximum growth, other factors being favourable, only when the available lime and magnesia are present in a ratio which may vary from 1:1 to 4:1. The authors have made observations on Porto Rican soils, and obtained very conflicting results, finding that soils with lime-magnesia ratios varying from 30:1 to 500:1 are productive pineapple soils; that one soil with the ratio 25:1 is an exceptionally productive soil for citrus fruits and pineapples; that another soil, where the ratio varies from 22:1 to 1461:1 is an exceptionally productive soil for sugar cane.

It may be that the apparently confirmatory results arrived at by some investigators are to be attributed rather to alterations in the soil reaction than to the lime-magnesia ratio. It would appear that in analyses of ordinary soils the above ratio is of no significance, but in analyses of the soluble salts of alkali soils the ratio may be exceedingly important.

T. S. P.

**Weathering of Soil.** G. H. LEOPOLD (*Chem. Weekblad*, 1913, 10, 70—86).—An investigation of the conditions affecting the formation of various types of soil by weathering, based on a large number of analyses of dark grey and red loams.

A. J. W.

**Two Volcanogenic Loams from Japan.** TOYOTARO SATO (*Landw. Versuchs-Stat.*, 1913, 79-80, 871—890).—Analyses of two loams from Tokio and from North-East Japan. The soils possess only a slight plasticity when kneaded with water, and are friable when dry. The soils do not contain zeolites, and their deficient plasticity is attributed to the absence of aluminium hydroxides and to the presence of allophanoids.

N. H. J. M.

## Organic Chemistry.

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**Some Data of the Solubility of Metallic Copper in the Different Fractions Obtained by the Distillation of Crude Petroleum.** CONSTANTIN I. ISTRATI and C. TEODORESCU (*Bull. Acad. Sci. Roumaine*, 1912/3, **1**, 19—25).—The requisite petroleum was obtained by fractionating crude petroleum taken from the Moreni reservoir. Eight fractions were collected, the extreme values of the b. p. being 100° and 300° respectively, each fraction having a range of b. p. of 25°. The separate fractions were placed in sunlight after addition of an excess of purely divided metallic copper. In general, the amount of copper salt formed increased with increasing b. p. of the fraction, the values observed varying from 0.022 gram per 100 c.c. for fraction b. p. 100—125° to 3.499 grams per 100 c.c. for fraction b. p. 275—300°. A notable exception to this regularity occurs with the portion of b. p. 250—275°, which dissolves less copper than either the preceding or succeeding fraction. Determination of the acidity of these fractions, whether by extraction with alcohol or by direct estimation with alcoholic potassium hydroxide, shows that this factor increases regularly with increasing b. p. of the fractions. The authors are led to the conclusion that this apparent anomaly is due to the presence of a larger proportion of lactones in the fraction b. p. 250—275°, which, although capable of neutralising alkali, are unable to attack metallic copper. This view is confirmed by the fact that a greater quantity of lactones can be extracted by means of alcohol from the fraction b. p. 250—275°, which has been treated with metallic copper, than from a similarly treated fraction, b. p. 225—250°. H. W.

**The Composition of Illuminating Gas.** PAUL LEBEAU and A. DAMIENS (*Compt. rend.*, 1913, **156**, 797—799).—Combining the ordinary methods of gas analysis with their own methods for analysing mixtures of gaseous hydrocarbons (this vol., ii, 253), the authors have made very complete analyses of three different samples of illuminating gas, and their results, which are tabulated, establish the presence of higher homologues of methane. Their values for carbon monoxide are somewhat lower than the generally accepted figure for that constituent. W. G.

**Mechanism of the Transformation of Stereoisomeric Ethylene Compounds.** RICHARD STOECKER (*Chem. Zentr.*, 1913, **i**, 93—931; from *Sitzungsber. Abh. Naturforsch. Ges. Rostock*, 1912, **4**, 35—43).—The transformation of stable ethylene compounds into labile stereoisomides by means of ultraviolet light (A., 1911, **i**, 235) cannot be explained by the theories of Wislicenus, Nef, or Aschan. July Werner's conception of the carbon atom offers any assistance, and his has now been developed so as to include *cis-trans*-isomerism in ring compounds. J. C. W.

VOL. CIV. i.

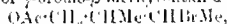
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**Elimination of Water from Pinacolyl Alcohol and on Tertiary Butylethylene.** W. FOMIN and N. SOCHANSKI (*Ber.*, 1913, 46, 1219. Compare this vol., i, 331).—The hexylene which Delacere obtained by the action of sodium on the chloride,  $\text{CMe}_2\cdot\text{C}(\text{Cl})\text{CH}_2$  (A., 1906, i, 476), was also *tert.*-butylethylene ( $\gamma\gamma$ -dimethyl- $\Delta^2$ -butylene). The hydrocarbon, "pseudo-butylethylene," b. p. 56–58°, which accompanied the  $\beta\gamma$ -dimethyl- $\Delta^4$ -butylene (Couturier, A., 1893, i, 244) had in the meantime been identified as  $\beta\gamma$ -dimethyl- $\Delta^2$ -butylene. J. C. W.

**Preparation of  $\beta\gamma$ -Dimethyl- $\Delta^2$ -butadiene.** BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 256717).—It is found that the yield of  $\beta\gamma$ -dimethyl- $\Delta^2$ -butadiene obtained from pinacone or pinacolm (A., 1911, i, 829) can be increased to 80% if the operation is carried out at 450° and under reduced pressure. F. M. G. M.

**Preparation of Diolefines.** BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 255519).—When monohalogenated olefines, dihalogenated paraffins or halogenated alcohols are heated at 300–500° at ordinary or reduced pressures with catalytic agents, such as barium chloride, nickel chloride, lead chloride or aluminium hydroxide, they furnish satisfactory yields of the corresponding diolefines, and the preparation of isoprene by this method from the following substances is now recorded.

From (1)  $\beta\gamma$ -dibromoisopentane,  $\text{CMe}_2\text{Br}\cdot\text{CHBrMe}$ , (2)  $\beta\gamma$ -dichloroisopentane, (3)  $\gamma\gamma$ -dibromoisopentane,  $\text{CMe}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , (4)  $\alpha\beta$ -dibromoisopentane,  $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , (5)  $\gamma$ -bromo- $\beta$ -methyl- $\Delta^2$ -butylene,  $\text{CMe}_2\cdot\text{CMeBr}$ , (6)  $\beta$ -chloro- $\beta$ -methylbutan- $\gamma$ -ol,  $\text{CMe}_2\text{CH}\cdot\text{CHMeOH}$ , (7) from the acetate of  $\gamma$ -bromo- $\beta$ -methylbutan- $\alpha$ -ol,



whilst  $\beta\gamma$ -dibromobutane,  $\text{CHMeBr}\cdot\text{CHBrMe}$ , furnishes divinyl, hexylene dibromide gives rise to hexadiene, b. p. 68–77°, and dodecene- $\alpha$ -pentane yields  $\Delta^2$ -pentadiene, b. p. 38–45°. F. M. G. M.

**The Action of Monosodioacetylene on the Alkyl Iodides.** Preparation of True Acetylenic Hydrocarbons. PAUL LERLET

and MAURIS PICOX (*Compt. rend.*, 1913, 156, 1077–1079).—Monosodioacetylene, prepared by the action of acetylene on sodium dissolved in liquid ammonia, when dissolved in the same solvent readily reacts with the alkyl iodides, giving the corresponding acetylene hydrocarbons in nearly theoretical yield. The ammonia is removed by absorption with water, the last traces being eliminated by dilute sulphuric acid. By this method the authors have prepared allylene and hexatriene. W. G.

**Preparation of Primary Alcohols by Reduction of the Esters with Absolute Alcohol and Sodium-ammonia.** E. CHARLAY (*Compt. rend.*, 1913, 156, 1020–1022).—Sodium in liquid ammonia reacts with esters of monobasic acids according to the equation:  $3\text{R}\cdot\text{CO}_2\text{R}' + 4\text{NH}_3\text{Na} = 2\text{R}\cdot\text{CONH}_2 + \text{R}\cdot\text{CH}_2\cdot\text{ONa} + 3\text{R}'\cdot\text{ONa} + 2\text{NH}_3$  (compare A., 1912, i, 244). Coupling this with the action of absolute alcohol on the sodium, giving nascent hydrogen, the

amide in its turn is converted into the corresponding primary alcohol, the whole of the acid being thus reduced to primary alcohol:  $2R(CO)NH_2 + 4H_2 = 2R \cdot CH_2OH + 2NH_3$ .

The ester dissolved in absolute alcohol is poured on to the solution of sodium in ammonia at  $-80^\circ$ . When the action is complete, the residue is decomposed by water, distilled in steam, and the mixture of alcohols separated by fractionation. The corresponding alcohols have thus been prepared from the esters of a number of the higher fatty acids. The esters of dibasic acids are similarly reduced, giving dihydroxy-alcohols; methyl sebacate gives decane- $\alpha$ -diol, m. p.  $71.5^\circ$ . Ethyl phenylacetate gives phenylethyl alcohol, whilst methyl cinnamate gives, not cinnamyl alcohol, but the saturated phenylpropyl alcohol.

W. G.

**New Methods of Spirit Rectification.** HUGO MASING (*Chem. Zeit.*, 1913, 37, 329—330).—It has hitherto been usual to dilute the raw spirit with water before submitting it to the process of rectification. It has been found in Russia, however, that better results are obtained when the undiluted spirit is used. In order to find out the reason, the author has constructed a special still-head, a modification of the Le Bel and Henninger form, in which there are taps to the side-tubes so that the liquid flowing from any one of the bulbs can be collected for analysis.

The results show that the strength of the spirit collecting in the bulbs increases more slowly than according to Gröhning's tables (compare A., 1908, i, 751), the slowest rate of increase being with the very dilute spirit. The Russian method of rectification is therefore justified.

T. S. P.

$\beta$ -Dimethylbutan- $\alpha$ -ol. ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 167—169).—Ethyl  $\alpha$ -dimethylacetate,  $C_6H_{12}O_2$  has b. p.  $148-150/745$  mm.,  $D_4^{20}$  0.8719,  $D_4^{25}$  0.8647,  $n_D^{20}$  1.4048.

$\beta$ -Dimethylbutan- $\alpha$ -ol,  $C_6H_{12}O$ , obtained by reducing the above ester by means of sodium in alcoholic solution, is a viscous liquid, b. p.  $114-145/761$  mm.,  $D_4^{20}$  0.8297,  $d_4^{20}$  1.4195, and forms a urethane,  $C_{13}H_{22}O_2N$ , m. p.  $28-29$ .

T. H. P.

**New Data Concerning the Oxide of Pentamethylene Glycol.** NICOLAI J. DEMJANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 169—173).—Since the action of nitric acid on pentamethylenediamine gives, in addition to pentamethylene glycol, a small proportion of an isomeric glycol, it is probable that the oxide obtained by the author (A., 1892, 1292) by heating pentamethylenediamine nitrite and by the action of sulphuric acid on the glycol prepared from pentamethylenediamine, and also that obtained by Hochstetter (A., 1903, i, 305) by the action of water on the bromide corresponding with the glycol from pentamethylenediamine, are not chemical individuals. Further, it is possible that the action of sulphuric acid on pure pentamethylene glycol may be accompanied by isomeric change, with formation of the oxide,  $O \begin{smallmatrix} \diagup CHMe \cdot CH_2 \\ \diagdown CH_2 \cdot \cdot \cdot CH_2 \end{smallmatrix}$ .

*à à 2*

The author has therefore prepared the pure oxide by heating pentamethylene bromide in a sealed tube. This oxide,  $C_5H_{10}O$ , is a liquid, b. p.  $86.5-87.5^\circ/743$  mm.,  $D_4^{20}$  0.883,  $D_4^{25}$  0.900,  $n_D^{20}$  1.4195, and on oxidation with nitric acid yields mainly succinic acid, its structure being thus confirmed. These properties agree closely with those given by Harries (A., 1911, i, 798) for his 3-methyltetrahydrofuran, and it may be that in the formation of this compound by the reduction of ethyl pyrotartrate, isomeric change occurs.

T. H. P.

**Development of Heat on Mixing Ether and Chloroform.** (Mme.) MARCLET and H. MARCELET (*Chem. Zentr.*, 1913, i, 229; from *Bull. Sci. Pharmacol.*, 1912, 19, 676-677).—Heat is developed when ether and chloroform are mixed, the maximum effect resulting from equal volumes; 25 c.c. of each liquid give a rise in temperature from  $16.6^\circ$  to  $30.3^\circ$ .

J. C. W.

**The Constitution of Sulphurous Acid.** WILHELM STROCKER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 126).—In continuation of previous investigations (A., 1910, i, 532), the sulphoxides have been prepared from symmetrical diethyl sulphite, and investigated optically. No details are given, but the conclusion arrived at from the optical results is, that there is no change in valency of the sulphur when a sulphoxide is oxidised into the sulphone; this is not in accordance with the chemical behaviour of these compounds.

T. S. P.

**Decomposition of Formates.** WILLIAM (ECHSNER DE CONINCK and ALBERT RAYNAUD (*Rev. Gen. Chim. pure appl.*, 1912, 15, 455-456).—When sodium formate is heated, a complex mixture of substances is evolved containing aqueous vapour, aldehydes (among which acetaldehyde has been identified, A., 1912, i, 527), oily substances, formic acid, and small quantities of carbon dioxide. The residue contains sodium carbonate, sodium hydroxide, and carbon.

Sodium, calcium, barium, potassium, and lead formates are decomposed to a greater or less extent when treated with pure methyl alcohol at its b. p. Formic acid was detected by distilling a portion of the alcohol and testing with silver nitrate solution after addition of water. When ethyl alcohol is substituted for methyl alcohol, very little decomposition is observed in the cases of sodium and calcium formates, whilst barium, potassium, and lead formates are rather more sensitive to the decomposing action of this reagent.

Solutions of lead formate, when exposed to diffused light during four months, are partly decomposed with the liberation of formic acid. Under similar conditions, uranium formate is completely decomposed in methyl-alcoholic solution within three months (compare this vol. i, 333).

H. W.

**Catalytic Esterification in Dilute Solutions: Preparation of Ethyl Acetate.** FERNAND BODROUX (*Compt. rend.*, 1913, 156, 1079-1081. Compare Sendzens and Aboulenc, A., 1911, i, 600, 637; ii, 1080; 1912, i, 694).—By distilling mixtures of ethyl alcohol and acetic acid diluted with water containing varying quantities of sulphuric

acid, ethyl acetate is obtained, the yield of the ester from given quantities of alcohol and acid varying with the amount of sulphuric acid in the water. With 10% sulphuric acid, a yield of 92% of ethyl acetate is obtained. The sulphuric acid can be replaced by numerous other acids as catalysts, but they are less effective. W. G.

**The Hydrolysis of Fats.** JULIUS MARCUSSEON (*Zeitsch. angew. Chem.*, 1913, 26, 173—176).—It is now generally accepted that the hydrolysis of fats in a homogeneous system takes place in steps with intermediate formation of diglycerides and monoglycerides (Fortini, A., 1912, i, 826; Grün and Corelli, A., 1912, i, 409; Fanto and Stritar, A., 1908, i, 499, and others). The present state of knowledge of the process of hydrolysis in a heterogeneous system, for example, by alkali, is not so satisfactory (compare Marcusson, A., 1906, i, 924; 1907, i, 674). Kellner (A., 1909, i, 357, 548, 759) obtained indications of a graded hydrolysis by superheated steam, but unfortunately used natural palm-kernel oil, which, as a mixture of triglycerides, might give misleading results. The author has investigated the hydrolysis of simple triglycerides, such as tribenzoin, tristearin, and tripalmitin, by heating with water in an autoclave; after this treatment the triglyceride had a m. p. several degrees lower, and in the case of the two latter fats, treatment with acetic anhydride (during which "aceto-lysis" did not occur; Willstätter and Madinaveitia, A., 1912, ii, 1104) gave a product which showed a considerably higher saponification number than the original triglyceride. Palm-kernel oil exhibited similar behaviour. From these results it appears that the hydrolysis of fats by water, and therefore presumably also by acids and enzymes, is a bimolecular process.

The author favours the view that the exceptional behaviour of alkali, which appears to hydrolyse directly to glycerol, is due to hydrolysis occurring mainly at the contact surface of fat and aqueous liquid; on account of the slow rate of diffusion of the intermediate diglycerides and monoglycerides, and the relatively great rapidity of their hydrolysis, no appreciable quantity of these substances can escape into the main body of fat again. In the above autoclave experiments, however, the elevated temperature increases the velocity of diffusion of the substances, whilst the hydrolysis is relatively much slower, so that the escape of the intermediate products from immediate further hydrolysis is facilitated. D. F. T.

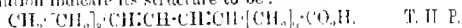
**Glycerides of Fats and Oils. IV. The Mixed Glycerides of Palmitic and Stearic Acids Obtained from Lard.** ALOIS BÜMER (*Zeitsch. Nahr. Genussm.*, 1913, 25, 321—353. Compare A., 1912, i, 600).—By repeated fractionation from ether, pure glycerides of saturated fatty acids were isolated from lard: the least soluble glyceride so obtained was found to be a palmityldestearin, and not heptadecyldestearin as stated by Kreis and Hafner. Tristearin is not present in lard. The palmityldestearin separated from lard had m. p. 68.5 (corr.), and differed in this respect and also in its crystalline form from the similar glyceride separated from mutton fat; the former is probably a palmityldestearin, whilst that from mutton fat is  $\beta$ -palmityl-



distearin. The lard under examination contained about 3% of  $\alpha$ -palmityldistearin, and about 2% of another saturated glyceride, namely, stearyldipalmitin, m. p. 58.2° (corr.). W. P. S.

**Glycerides of Fats and Oils. V. Nomenclature of Mixed Glycerides and the Synthesis of  $\alpha$ -Distearin and  $\beta$ -Palmityldistearin.** ALON BÄGER and R. LUXERICH (*Zeitsch. Natur. Genussm.*, 1913, 25, 351—366).—It is suggested that, in the case of mixed glycerides, where different fatty acid radicles are combined with the same glycerol molecule, the position of the fatty acid radicles should be denoted by the letters  $\alpha$ ,  $\beta$ , and  $\gamma$  respectively. In the preparation of  $\alpha$ -distearin from  $\alpha$ -dichlorohydrin and potassium stearate (compare A., 1903, i, 788), considerable quantities of tristearin are also formed; again, tristearin and possibly stearyldipalmitin are produced together with  $\beta$ -palmityldistearin when the latter is prepared from  $\alpha$ -distearin and palmitic acid.  $\alpha$ -Distearin has m. p. 78.5° (corr.), and  $\beta$ -palmityldistearin has m. p. about 63°, and is identical with the palmityldistearin separated from mutton fat. W. P. S.

**China Oil.** SERGEI A. FORIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 283—285).—The polymerisation of this oil when heated, the increased refraction, and the transformation of the elcomargaric acid under the influence of light into a product with a higher melting point are explainable on the assumption that the acid contains either conjugated double linkings or, as in allene, a carbon atom with two double linkings. The products obtained when the acid is oxidised with alkaline permanganate solution indicate its structure to be:



**Behaviour of Certain Unsaturated Acids Towards Selenious Acids.** SERGEI A. FORIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 285—286).—Various unsaturated aliphatic acids and, more especially, the oils containing them as glycerides, undergo marked changes when heated with concentrated solutions of selenious acid at 160° under the ordinary pressure. This action is most characteristic in the case of castor oil. After one to three hours' heating, the oil becomes converted into a croutchou-like mass of a faint red colour. This product is insoluble in alcohol, ether, benzene, pyridine, etc., but it dissolves with decomposition in boiling acetic acid, and is saponified and darkened by alcoholic potassium hydroxide. When treated with alcohol or ether, it swells to a jelly, which can be readily pounded to a paste and, after evaporation of the alcohol or ether in the cold, reduced to powder. After being washed to remove any excess of selenious acid or castor oil, the powder has the iodine number 59.0 and the saponification number 168.5, the corresponding numbers for castor oil being 56 and 180 respectively. The substance contains selenium, and the presence of double linkings and the small difference between its saponification number and that of the original oil indicate it to be different from the "factin" obtained by the action of sulphur dioxide tetrachloride on linseed and other oils. T. H. P.

**Formation, Decomposition, and Transformation of Glycollic Acid.** ERIC BAUR (*Ber.*, 1913, **46**, 852--863).—It is found that the reduction of oxalic acid to glycollic acid which can be effected by electrolytic reduction with lead, or less well with platinum, cathodes (A., 1908, i, 600), also occurs to some extent when a solution of oxalic acid with formic acid is submitted to the action of finely divided rhodium (Schade, A., 1908, i, 136; Blackadder, this vol., ii, 36) or of platinised platinum foil. The metal causes the decomposition of the formic acid into hydrogen and carbon dioxide, the former of which effects a reduction of the oxalic acid through glyoxylic acid to glycollic acid. Small quantities of the two last substances can be detected in the final mixture.

In the presence of coloured metallic salts, glycollic acid is affected by exposure to the light of a quartz mercury lamp, being partly converted into formaldehyde and formic acid. The following salts, copper sulphate, manganic and manganous sulphates, and ferric sulphate all exerted this effect, but the first-named was least active and the last-named most.

When tubes of quartz glass containing an aqueous solution of calcium glycolate or of a mixture of calcium glycolate and calcium malate are submitted to the light of a quartz-mercury lamp for one hundred and forty hours, a certain amount of calcium citrate is formed (compare Camician and Silber, A., 1911, i, 513, 650); the same condensation to citric acid occurs when saturated solutions of calcium glycolate or calcium malate, mixed with one and a-half times their bulk of saturated lime water, are kept for a few days. Although it was not possible to prove the presence of a malate in the solution of calcium glycolate after exposure to light, the accidental growth of a mould in a solution of calcium glycolate caused the formation of minute crystals of calcium malate.

In connexion with his view that oxalic acid is the first product of assimilation of carbon dioxide in plants (A., 1908, ii, 789), the author draws attention to the manner in which the above results render oxalic acid a possible origin of the common vegetable acids; further, by its scission into formaldehyde and formic acid, glycollic acid may possibly be the source of the sugars.

D. F. F.

**Method of Preparing Ethyl  $\gamma$ -Chloroacetoacetate.** DIMITRI K. ALEXANDROV (*Ber.*, 1913, **46**, 1021--1024).—By the interaction of magnesium powder with ethyl  $\alpha$ -chloroacetate, a condensation product of two molecules,  $(\text{CH}_3\text{CHClCH}_2\text{CO}_2\text{Et})_2\text{Mg}$ , is formed, which is decomposed by water into ethyl  $\gamma$ -chloroacetoacetate. This is a colourless oil, b. p. 107–114 mm., giving a red coloration with ferric chloride, D. 1.2157,  $n_D^{20}$  1.4516. The copper salt crystallises in thin, matted, pale green needles, m. p. 168–169 (decomp.).

E. F. A.

**Action of Oxalyl Chloride on Several Organic Derivatives.** HERMAN J. TAVERNE (*Chem. Weekblad*, 1913, **10**, 214–225. Compare Grassie and Liebermann, *Ber.*, 1869, **2**, 678; Seidinger, A., 1908, i, 258, 1909, i, 736, 995; 1912, i, 567; Jones and Tasker, E., 1909, 95, 1904; Liebermann and Zoffa, A., 1911, i, 202;

Liebermann, A., 1911, i, 656; 1912, i, 464; Bornwater, A., 1911, i, 616).—A summary of work on the reactions of oxalyl chloride previously published.

A. J. W.

**Solubility of Thorium Oxalate.** A. COLANI (*Compt. rend.*, 1913, 156, 1075—1076. Compare Wirth and Hanser, A., 1912, i, 827).—A study of the solubility of thorium oxalate, alone or in the presence of oxalic acid, in hydrochloric acid at 17° and 50°. For varying concentrations of hydrochloric acid, the amount of oxalate dissolved is independent of the amount in contact with the liquid. With moderately strong acid, the oxalate is converted into chloro-oxalate with the elimination of oxalic acid, which consequently diminishes the solubility of the chloro-oxalate. The solubility of the thorium oxalate in hydrochloric acid is greatly diminished by the presence of small amounts of oxalic acid.

W. G.

**Preparation and Properties of the Ammonium Salts of Some Organic Acids.** LEROY McMASTER (*Amer. Chem. J.*, 1913, 49, 294—301).—Keiser and McMaster (this vol., i, 248) have described a method for the preparation of normal ammonium salts of dibasic organic acids. In continuation of this work, ammonium malonate, succinate, malate, tartrate, phthalate, and isophthalate have been prepared. The method has also been used for obtaining the salts of certain monobasic acids, and ammonium propionate, isobutyrate, palmitate, benzoate, and cinnamate are described.

E. G.

**Crystalline Form and Optical Properties of Magnesium Malate.** O. I. MOROSCHINA (*Bull. Acad. Sci. St. Petersburg*, 1913, 225—230).—Magnesium malate,  $Mg(C_4H_4O_5)_2 \cdot 5H_2O$ , crystallises in hemihedral forms of the rhombic system:  $a:b:c = 0.7476:1:0.496$  (compare Trambé, A., 1899, i, 484). The etched figures and optical properties are described.

T. H. P.

**Tetrolaldehyde ( $\Delta^6$  Butinal) and Some of Its Derivatives.** PAUL L. VIGIER (*Ann. Chim. Phys.*, 1913, [viii], 28, 433—536).—A résumé of the work accomplished, and already abstracted, on this subject since 1908.

T. A. H.

**Catalytic Hydrogenation of Acetone.** A. LASSIEUR (*Compt. rend.*, 1913, 156, 795—797. Compare Haller and Lassieur, A., 1910, i, 355).—The hydrogenation of acetone by the method of Sabatier and Senderens at temperatures above 200° yields neither isopropyl alcohol nor a pincone, but the principal product is methyl isobutyl ketone, together with a small quantity of valerone and some still more highly condensed products.

W. G.

**Migration of the Chlorine in the Halogenated Ketones** EDMOND E. BLAISE (*Compt. rend.*, 1913, 156, 793—795. Compare this vol., i, 11).—By the chlorination of methyl ethyl ketone in the presence of water and marble a mixture of three chlorinated ketenes is obtained. The smallest fraction is dichloromethyl ethyl ketone, b. p. 31°.

23–34 mm. The second and largest fraction is chloromethyl  $\alpha$ -chloroethyl ketone, b. p. 165° (compare Vladesco, A., 1892, 424). The third constituent is methyl  $\alpha$ -dichloroethyl ketone (compare Favorski and Desbout, A., 1895, 497). On heating dichloromethyl ethyl ketone with a mixture of hydrochloric and acetic acids on a water-bath for six hours, 50% of it is converted into chloromethyl  $\alpha$ -chloroethyl ketone, one of the chlorine atoms having migrated. Increase in the amount of hydrochloric acid in the mixture facilitates the migration. W. G.

**Reduction of Acetobromoglucose and Similar Substances.** EMIL FISCHER and KARL ZACH (*Sitzungsber. K. Akad. Wiss. Berlin.* 1913, 311–317).—On reduction of acetobromoglucose by means of zinc dust and acetic acid at the ordinary temperature, a crystalline compound,  $C_{12}H_{20}O_7$ , is obtained, together with a molecule of acetic acid. The new compound, *acetoglucal*, takes up two atoms of bromine. On hydrolysis three molecules of acetic acid are eliminated, and *glucal*,  $C_{12}H_{18}O_6$ , a soluble viscid syrup, b. p. 170–185°/0.2 mm. pressure, is obtained. This behaves as an aldehyde, and forms oily hydrazones, but no osazones. It decolorises bromine in aqueous solution, and is decomposed by acids, giving an intense green pine-splinter reaction when heated with hydrochloric acid.

Provisionally the formula  $\begin{array}{c} \text{CH-CH(CH}_2\text{-OH)} \\ | \\ \text{CH-CH(CHO)} \end{array} > \text{O}$  is suggested.

Acetobromogalactose and acetobromolactose behave similarly when reduced, but only oily products were obtained.

*Acetoglucal* has m. p. 51–55°,  $[\alpha]_D^{20} = 13.62^\circ$ .

E. F. A.

**Phytin.** R. H. ADERS PLIMMER and HAROLD J. PAGE (*Biochem. J.* 1913, 7, 157–174).—Inorganic phosphates in phytin can be estimated by precipitation with ammonium molybdate in semi-normal nitric acid at room temperature. The calcium can be estimated by precipitation as calcium sulphate, but not as oxalate. The magnesium can then be estimated as pyrophosphate. There is great difficulty in removing the calcium from phytin in the preparation of phytic acid. The yield of inositol on hydrolysis of the latter is not quantitative; there is possibly another organic constituent in phytin. W. D. H.

**Transformation of *l*-Arabinose into *l*-Ribose.** WILLIAM ALBERTA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1913, 10, 213–214).—Heating with dilute aqueous sodium hydroxide partly converts *l*-arabinose into *l*-ribose, the presence of the latter in the mixture being proved by oxidising the two pentoses to arabonic acid and ribonic acid, converting these acids into their phenylhydrazides, and separating the hydrazides by fractional crystallisation.

A. J. W.

**Action of Hydrogen Peroxide and Ferric Chloride on Starch.** O. DURIEX (*Bull. Soc. chim. Belg.*, 1913, 27, 90–97. Compare Neuberg and Miura, A., 1911, 1, 955; Gerber, A., 1912, 1, 538).—Hydrogen peroxide solution does not hydrolyse soluble starch prepared by Fernbach's method at the ordinary temperature, and the

same is true of colloidal solutions of iron or of mixtures of these two products. Similarly, a solution of ferric chloride does not hydrolyse starch, but when used along with hydrogen peroxide it causes hydrolysis at an appreciable rate, which increases with the quantity of ferric chloride employed. The results of experiments designed to test the influence of various factors on the reaction show that the quantity of reducing substances formed depends on the quantity of peroxide used, and that the acidity of the mixture increases with the quantity of reducing substances formed. The hydrogen peroxide is decomposed, but no oxygen is evolved unless the peroxide is present in excess. The iron remains in the ferric state until hydrolysis is complete, when it suffers reduction, the reducing substances disappearing at the same time. Measurements of the rate of hydrolysis show that the reaction does not follow the logarithmic law for a unimolecular reaction. Hydrogen peroxide reduces the rate of hydrolysis of starch by diastase and does not undergo decomposition itself. T. A. H.

**Starch of Glutinous Rice and Its Hydrolysis by Diastase.** YOSHIO TANAKA (*J. Ind. Eng. Chem.*, 1912, 4, 578-581).—The starch of glutinous rice is characterised by giving a red coloration with iodine; the microscopic characteristics of these starch granules and the hydrolysed products do not apparently differ in any way from those of common rice starch. The starch of glutinous rice does not contain amylopectin, erythropectin, or the special proteins which have previously been considered to be the cause of the red iodine coloration; nor does it contain any of the common starch, which gives a blue colour with iodine.

Glutinous rice starch is, moreover, rapidly hydrolysed by diastase to dextrin with the production of a less amount of maltose than in the case of equal quantities of potato or common rice starch; the author considers that glutinous rice starch contains a larger amount of amylopectin, or some analogous constituent which produces a dextrin that hydrolyses more slowly with diastase than does that from ordinary starch.

It is probable that there are many other cereals in Nature containing a similar variety of starch, its presence having been noted in glutinous millet, glutinous *Panicum miliaceum*, L., and in *Andropogon Sorghum*. The separation of glutinous from common rice starch is comparatively simple, as the former is opaque, the latter translucent.

F. M. G. M.

**The Acetolysis of Cellulose to Dextrose Acetate.** HERMANN OST (*Arch. int. deut. Veterinärmed. Gesell.*, 1913, 124-125).—The end-product of the acetylation of cellulose is cellobiose octa-acetate (compound A., 1912, 1, 686), which is readily obtained in a pure crystalline condition when a mixture of 5 grams of cellulose with 25 c.c. of acetic anhydride and 25 grams of concentrated sulphuric acid is kept at the room temperature for some days, or even weeks; the yield is 35. The reaction proceeds further on warming. For example, a mixture of 5 grams of cellulose, 25 c.c. of acetic anhydride, 25 c.c. of glacial acetic acid, and 5 grams of concentrated sulphuric acid when heated

for three days at 45° no longer gives cellobiose octa-acetate; by extraction with ether, a syrup consisting of a mixture of dextrose penta-, tetra-, and tri-acetates is obtained, which by further acetylation can be transformed into dextrose  $\alpha$ -penta-acetate, m. p. 112°, and a rotation of +161.7°. The same product can be obtained directly from cellobiose octa-acetate.

The results confirm the conclusion already drawn by Ost and Wilkening that the cellulose molecule is built up exclusively from dextrose residues.

T. S. P.

**Nitrocellulose.** H. TEDESCO (*Zeitsch. ges. Schiess-Sprengstoffwesen*, 1912, 7, 174—477).—An account of numerous experiments on various methods of preparing nitrocellulose, with special regard to the varying nitrogen content and stability of the products obtained under different conditions, such as varying the relative concentrations of the acids employed, the time allowed, and the temperature at which nitration is carried out, and employing different forms of cellulose for the experiments.

F. M. G. M.

**Soil Humus.** SHERMAN LEAVITT (*J. Ind. Eng. Chem.*, 1912, 4, 601—604).—Two methods of preparing samples of humus are fully described, and the following facts are emphasised.

(1) Two methods were employed for the removal of clay: (a) Mooers and Hampton's method; (b) mechanical separation without evaporation to dryness.

(2) Indications were obtained of the relative behaviour of ferric iron, ferrous iron, and calcium in the retention of humus from water solution.

(3) Protein or protein-like substances were pre-ent in the humus examined.

(4) A starch-like substance was present which can be hydrolysed by acids, acted on by diastase with subsequent acid hydrolysis, and both processes gave reducing sugars in comparable amounts in all samples of humus examined.

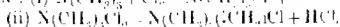
(5) One of these reducing sugars was obtained in crystalline form, but has not yet been fully identified.

(6) Pento-ans were present in appreciable amounts in all samples of humus examined.

(7) Nitrogen, pre-ent probably as an amino-acid, was found in the 1% hydrochloric acid extract in all soils examined by the official method.

F. M. G. M.

**Action of Hypochlorous Acid on Tertiary Amines.** JAKOB MEISENHEIMER (*Ber.*, 1913, 46, 1148—1161).—Willstätter and Jglauer (*A.*, 1906, i, 458) have shown that dialkylchloroamines are formed by the action of hypochlorous acid on tertiary amines (compare also Hantzsch and Graf, *A.*, 1905, i, 575). The authors have applied the reaction to simple tertiary amines, and are led to the conclusion that a trialkylamine dihydrochloride is first formed, which rapidly decomposes with elimination of hydrogen chloride according to the scheme for trimethylamine: (i)  $N(CH_3)_3 + Cl_2 \rightarrow N(CH_3)_2Cl + HCl$ ;



Dimethylmethylene ammonium chloride becomes transformed into formaldehyde and dimethylamine hydrochloride, the latter finally reacting with excess of hypochlorite, yielding dimethylchloroamine. This explanation differs from that given by Willstätter or Hantzsch in that two molecules of hypochlorous acid are required for each molecule of amine instead of one, and thus accounts for the fact that Willstätter and Iglauer obtained the best yields of chloronortropidine only by the use of two or more molecules of hypochlorous acid. Further, it involves the formation of aldehydes instead of alcohols as secondary products, and the production of large quantities of formaldehyde or acetaldehyde during the action of sodium or calcium hypochlorite on trimethylamine or triethylamine has been experimentally proved. Such aldehydes must be directly formed, since, under the conditions employed, alcohols are not oxidised to aldehydes. The assumption of the primary addition of chlorine appears at first sight to be improbable, since free chlorine does not convert tertiary amines into dialkylchloroamines to an appreciable extent. This is explained by the fact that two molecules of a tertiary amine are converted by one molecule of chlorine into a mixture of the hydrochlorides of the tertiary and secondary amines:



and that free chlorine does not react with salts of amines in the same manner as with the free amines.

No action occurs when the hydrochlorides of trimethylamine or triethylamine are mixed with aqueous solutions of free hypochlorous acid. With the free amines, dialkylchloroamines are formed in small quantity. Good yields of the latter substances can only be obtained by employing sodium hypochlorite or, better, bleaching powder.

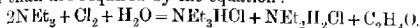
An aqueous solution of triethylamine hydrochloride was added to a cooled suspension of bleaching powder in water. On distillation, a mixture of dimethylchloroamine and methylchloroamine was obtained, the latter being derived from decomposition of the former. Formaldehyde remained chiefly in the residue, and was identified by precipitation with *p*-nitrophenylhydrazine. Good yields of chloroamine were only obtained when a large excess of bleaching powder was used. Employment of sodium hypochlorite led to similar results. The yields, however, were uniformly less, and the best experimental conditions less readily ascertained. Nitrogen, nitric acid, and tetramethylammonium chloride were not formed.

Triethylamine hydrochloride in aqueous solution was similarly converted by an aqueous suspension of bleaching powder into a mixture of diethylchloroamine and ethylchloroamine, which possibly contained a small quantity of chloroform. A large excess of bleaching powder was necessary, since, otherwise, the yields of chloroamine became very small. On the other hand, a portion of the triethylamine became then converted into diethylamine as was shown in experiments with sodium hypochlorite.

Triethylamine hydrochloride did not react with chlorine water, which, however, was decolorised by dimethylamine hydrochloride.

The reaction between triethylamine and chlorine water has been investigated. When the former was distilled into the latter, smaller

quantities of diethylamine hydrochloride and acetaldehyde were obtained than are required by the equation:



The authors consider that acid is formed in by-reactions which converts the tertiary amine into the corresponding salt, which is not acted on by chlorine. In a subsequent experiment, in which the amine was added in one portion to the chlorine water, a somewhat larger amount of aldehyde was detected. H. W.

**Preparation of Betaine from Molasses Residues.** KARL URBAN (*Zeitsch. Zuckerind. Böhm.*, 1913, 37, 339—341).—To obtain betaine the evaporated molasses residues are mixed with an equal volume of concentrated hydrochloric acid. After cooling, the alkali chlorides which have separated are removed by filtration, and the filtrate is evaporated in a porcelain dish. The volatile organic acids and hydrochloric acid pass away, and humus substances are precipitated. These are also filtered off, and the residue further evaporated to a thick syrup. This is dissolved in water, filtered, decolorised by means of charcoal, and concentrated, when betaine hydrochloride separates out in a nearly pure state. E. F. A.

**Chemical Reactions Brought About by Sunlight.** DOMENICO GANASSINI (*Chem. Zentr.*, 1913, i, 153—154; from *Giorn. Farm. Chim.*, 1912, 61, 439—444, 481—491).—Aqueous solutions of some mono- and di-basic amino-acids have been exposed to sunlight for three or four days, then treated with an excess of magnesium oxide, and left with red litmus paper. This soon became blue, whereas solutions which had been kept in the dark were without action. It was shown that glycine, alanine, asparagine, aspartic acid, and glutamic acid gradually decomposed into the corresponding aldehyde, ammonia, and carbon dioxide. J. C. W.

**Synthesis of the Natural Hydroxyproline Present in Proteins. Pyrrolidine Derivatives. IV.** HERMANN LEUCHS and JOSEPH F. BREWSTER (*Ber.*, 1913, 46, 986—1000).—The preparation of hydroxyproline has been improved by treating  $\alpha\delta$ -dichlorovalerolactone with ammonia instead of  $\delta$ -chloro- $\alpha$ -bromovalerolactone.

$\gamma$ -Hydroxyproline-(a)-phenylcarbimide is resolved by means of quinine. The synthetic  $\gamma$ -hydroxyproline derivative has  $[\alpha]_D^{25} - 37.0^\circ$ , whereas the natural product has  $[\alpha]_D^{25} - 37.2^\circ$ . This synthesis confirms the  $\gamma$ -position of the hydroxy-group and the structure assumed for the natural hydroxyproline.

The phenylcarbimide of hydroxyproline-(b) is also resolved by means of quinine, the ammonium salt having  $[\alpha]_D^{25} \pm 45^\circ/d$ . The active acid could not be obtained crystalline, but the corresponding hydantoins crystallise without difficulty.

To convert the  $\gamma$ -hydroxyproline-phenylcarbimide into the corresponding amino-acid, heating with concentrated hydrochloric acid in a sealed tube at  $95^\circ$  is necessary, but the product has lost its optical activity. To preserve this, the heating is carried out at  $95^\circ$  with aqueous ammonia, when  $\gamma$ -hydroxyproline and phenylcarbimide are



obtained. The synthetic *l*-hydroxyproline has  $[\alpha]_D^{20} = -76.3^\circ$ , whereas the only value available for the natural acid is  $-81^\circ$ .

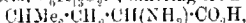
The *quinine* salt of *hydroxyproline-phenylcarbinide* crystallises in needles or thin prisms, m. p.  $206-209^\circ$  (decomp.),  $[\alpha]_D^{20} = -37.2^\circ$ .

The corresponding *hydantoin* also crystallises in needles or thin prisms, m. p.  $122-123^\circ$ ,  $[\alpha]_D^{20} = -50.4^\circ$ .

*l*- $\gamma$ -*Hydroxyproline-phenylcarbinide*-(a) has m. p.  $175^\circ$ .

The corresponding derivative of  $\gamma$ -hydroxyproline-(b) does not crystallise, but the *hydantoin* forms lustrous, oblique prisms, m. p.  $156-158^\circ$ ,  $[\alpha]_D^{20} = -55.2^\circ$ . E. F. A.

**A New Amino-acid of the Composition  $C_6H_{13}O_2N$  Obtained by the Total Hydrolysis of the Proteins of the Nerve Substance.** EMIL ABERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1913, 84, 39-59. Compare A., 1912, ii, 1191).—The leucine fraction of the products of the complete hydrolysis of nerve proteins contains an amino-acid,  $C_6H_{13}O_2N$ , differing from either leucine,

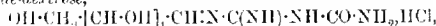


or *isoleucine*,  $CHMeEtCH(NH_2)CO_2H$ , which is regarded as *d*-amino-hexoic acid,  $CH_3[CH_2]_3CH(NH_2)CO_2H$ , and termed *caprine*. The existence of this isomeride in the nerve proteins was suggested by Thudichum, who did not determine its constitution. It is probable that it is present in other proteins. The ester of *d*-caprine has b. p.  $91^\circ/12$  mm. *d*-*Caprine* itself has decomp.  $285^\circ$ ,  $[\alpha]_D^{20} = +6.53^\circ$  in water, and  $+11.1^\circ$  in 20% hydrochloric acid, and tastes faintly sweet. The corresponding *hydroxy-acid* crystallises in long, four-angled plates, m. p.  $57^\circ$ ,  $[\alpha]_D^{20} = +4.68^\circ$ . The same acid prepared from the synthetic amino-acid forms slender, needle-shaped prisms, m. p.  $66^\circ$ ,  $[\alpha]_D^{20} = +2.17^\circ$ , whereas the corresponding hydroxy-acid from *l*-leucine has m. p.  $71^\circ$ ,  $[\alpha]_D^{20} = +16.37^\circ$ . E. F. A.

**Compounds of Guanylecarbamide and Guanylguanidine with Dextrose.** LEOPOLD RADLERGER (*Chem. Zentr.*, 1912, ii, 1963-1964 from *Österr. ung. Zeitsch. Zucker-Ind. Landw.*, 1912, 41, 745-750).—Guanylecarbamide (dicyanodiamidine) forms a *chloride*,  $C_4H_5ON_4Cl_2 \cdot \frac{1}{2}H_2O$ , which is obtained in thin, colourless leaflets by evaporating the solution in concentrated hydrochloric acid over lime. The aqueous solution is neutral, and when rendered alkaline and boiled with a few drops of copper sulphate solution, develops a violet colour and deposits a rose-red powder,  $C_4H_5O_2N_4Cu$ , on cooling. Guanylguanidine (biguanide), may be purified by recrystallisation from alcohol (compare Bamberger and Dieckmann, A., 1892, 737). The chloride has the formula



The chlorides condense with dextrose in alcoholic solution. *Guanylguanidine-dextrose*,



forms slender, microscopic needles, m. p.  $107^\circ$  (decomp.),  $\alpha_D^{20} = +0.2$  (2% solution in alcohol, 2-dm. tube), which reduce Fehling's solution and respond to the above test for guanylecarbamide. *Guanylguanidine-dextrose*,  $OH \cdot CH_2[CH(OH)]_4 \cdot CHN \cdot C(NH) \cdot NH \cdot C(NH) \cdot NH_2 \cdot 2HCl$ , forms small needles which sinter at  $116^\circ$ , have a bitter taste, reduce

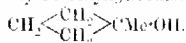
Fehling's solution, and give red needles of cuproguanido sulphate with ammoniacal copper sulphate. A 2% alcoholic solution in a glass tube gives  $n_D^{20} + 0.5^\circ$ . J. C. W.

**Action of Sulphuric Acid on Dicyanodiamide.** Correction. Hjalmar LIDHOLM (*Ber.*, 1913, 46, 1218. Compare this vol., i, 252).—The formula for dicyanodiamide was suggested by Bunberger (A., 1883, 907) and not by Pohl, and the reduction to guanidine was accomplished by Bunberger and Seeborg (A., 1893, 491). J. C. W.

**Colour Changes in Solutions of Cobaltous Thiocyanate.** RAUL WERNICKE (*Anal. Soc. Chim. Argentina*, 1913, 1, 8–32).—Pure cobaltous thiocyanate was obtained by the action of an excess of the sulphate on alcoholic potassium thiocyanate, and repeated extraction and crystallisation of the cobalt salt by alcohol. Data of the conductivity and viscosity are given. The phenomena of colour-change are in general similar to those shown by the chloride. G. D. L.

**Reduction of Sodium Nitroprusside by Hydrogen Sulphide.** DOMENICO VENDITORI (*Atti R. Accad. Lincei*, 1913, vi, 22, i, 162–167. Compare A., 1906, i, 486).—The reduction was effected by the action of an excess of hydrogen sulphide on a 10% solution of sodium nitroprusside kept on a water-bath for five or six hours. Hydrogen cyanide is evolved, and ultimately there results a solution (of nitrosulphide and ferrocyanide) and a precipitate (of sulphur and complex iron cyanogen compounds). As to the soluble products, 100 parts of nitroprusside yield about 13 parts of the nitrosulphide,  $\text{Na}[\text{Fe}(\text{NO})\text{S}_2]$ , and about 42 parts of sodium ferrocyanide. The yellowish-white precipitate becomes blue on exposure to the air; the yield of it is about 33% of the nitroprusside taken. When it is treated with warm concentrated hydrochloric acid, a blue powder remains undissolved, whilst the solution contains a green substance which can be reprecipitated with water. It is uncertain whether the acid effects a separation or induces a further reaction. The original crude precipitate seems to have a constant composition. R. V. S.

**Vinyleclop propane and its Derivatives.** NICHOLAI J. DEMJANOV and M. DOBARENKO (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 176–181).—By various methods Gustavson (A., 1886, i, 609) obtained from vinyltrimethylene an alcohol, b. p. 115–118°. This alcohol is of tertiary character, and from the value of its optical exaltation and from the fact that its boiling point exceeds that of dimethylethylcarbinol by 15°, which is also the difference between the boiling points of  $\beta$ -methylbutyl alcohol and cyclohexylcarbinol, the authors conclude that it is probably 1-methyleclobutan-1-ol,



and not 1-ethyleclop propane-1-ol.

The alcohol is converted by the action of hydriodic acid first into the iodide,  $\text{C}_5\text{H}_{11}\text{I}$ , b. p. 50.22 mm., 55/50 mm.,  $D_4^{20} + 1.603$ , and

subsequently into the iodide,  $C_7H_{10}I_2$ . Reduction of the iodide,  $C_7H_{10}I_2$ , by means of zinc dust and acetic acid yields (1) *ethylcyclopropane*,  $\frac{CH_3}{CH_2} > CHEt$ , b. p. 34—35°, 753 mm.,  $D_4^{20}$  0.6973,  $D_4^{25}$  0.6371,  $D_4^{27}$  0.6805,  $n_D^{25}$  1.3814, which is also obtained on reducing *vinylcyclopropane* by means of hydrogen in presence of platinum black, and (2) an ester,  $C_7H_{14}O_2$ , of the original alcohol and acetic acid.

T. H. P.

Terpenes and Ethereal Oils. CXIV. Alicyclic Unsaturated Hydrocarbons. OTTO WALLACH (*Annalen*, 1913, 396, 264—284).—

4-Methylcyclohexan-1-ol and magnesium methyl iodide yield by the usual method 1:4-dimethylcyclohexan-1-ol, which is converted by boiling dilute sulphuric acid into 1:4-dimethyl- $\Delta^1$ -cyclohexene, b. p. 127—128°,  $D_4^{20}$  0.8020,  $n_D^{20}$  1.4459. By oxidation with 1% potassium permanganate at 0°, the latter is converted into 1:4-dimethylcyclohexane-1:2-diol, m. p. 77°, which yields 1:4-dimethylcyclohexan-2-one by treatment with dilute sulphuric acid. 1:4-Dimethyl- $\Delta^1$ -cyclohexene forms a *nitrosochloride*, m. p. 83—84°, which is easily volatile with steam, forms a *nitrolpiperidine*,  $C_7NH_{10}CMe \begin{smallmatrix} C(NOH)CH_2 \\ | \\ CH_2-CH_2 \end{smallmatrix} CHMe$ , m. p. 169—170°, and is converted into 1:4-dimethyl- $\Delta^2$ -cyclohexen-2-oneoxime by loss of hydrogen chloride.

1:3-Dimethylcyclohexan-3-ol is converted by boiling dilute sulphuric acid into 1:3-dimethyl- $\Delta^3$ -cyclohexene, b. p. 127.5—128.5°,  $D_4^{20}$  0.8025,  $n_D^{20}$  1.4466, which forms a *nitrosochloride* (the *nitrolpiperidine* has m. p. 130—131°) extremely slowly, and is oxidised to 1:3-dimethylcyclohexane-3:4-diol by 1% potassium permanganate.

By careful fractional distillation with an efficient column, it can be shown that the liquid obtained by the auto-condensation of methylheptenone in the presence of zinc chloride or phosphoric oxide, and hitherto regarded as pure dihydro-*m*-xylene, contains 1:3-dimethyl- $\Delta^3$ -cyclohexene. Also when methylheptenone is treated with 75% sulphuric acid, the product is shown to be a mixture of 1:3-dimethyl- $\Delta^3$ -cyclohexene and *m*-xylene.

1:2-Dimethylcyclohexan-1-ol and boiling dilute sulphuric acid yield 1:2-dimethyl- $\Delta^1$ -cyclohexene, b. p. 135—137° (Sbatier gives 132°),  $D_4^{20}$  0.824,  $n_D^{20}$  1.4587, which forms a *nitrosochloride*, m. p. 58—60°, colourless when solid, blue when liquid, from which an oxime cannot be obtained. The unsaturated hydrocarbon forms a *di bromide*, m. p. 154—156°, and a *glycol*, m. p. about 38—39°, by oxidation.

[With L. AUGSPERGER.]—By warming with dilute sulphuric acid, 4-methyl-1-ethylcyclohexan-1-ol yields chiefly 4-methyl-1-ethyl- $\Delta^1$ -cyclohexene, b. p. 153—154°,  $D_4^{22}$  0.8145,  $n_D^{20}$  1.4514, which forms a *nitrosochloride* consisting of two stereoisomeric modifications, one having m. p. 103—104° and being sparingly soluble in acetone or petroleum, the other having m. p. 98—99° and being easily soluble. Both modifications yield the same *nitrolpiperidine*, m. p. 134°, and by loss of hydrogen chloride the same *oxime*, m. p. 59—60°. By oxidation with dilute potassium permanganate, 4-methyl-1-ethyl- $\Delta^1$ -cyclohexene is

converted into 4-methyl-1-ethylcyclohexane-1:2-diol, m. p. 76—77°; the constitution of which is proved by its conversion into 4-methyl-1-ethylcyclohexan-2-one.

[With HANS SCHLUBACH.]—1:3:5-Trimethylcyclohexan-1-ol, b. p. 181°; prepared from 3:5-dimethylcyclohexan-1-one and an excess of magnesium methyl iodide, is converted by boiling 50% sulphuric acid into 1:3:5-trimethyl- $\Delta^1$ -cyclohexene, b. p. 142.5—143.5°,  $D_{20}^{25}$  0.7965,  $n_D^{25}$  1.4447, which forms a nitrosochloride, m. p. 134° (nitro! piperidide, m. p. 122—123°), and is oxidised to 1:3:5-trimethylcyclohexane-1:2-diol, m. p. 104°, by cold dilute potassium permanganate. C. S.

**Preparation of Partly Hydrogenised Cyclic Hydrocarbons.** BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 255538. Compare this vol., i, 349).—When dichlorocyclohexane is heated at 350—450° and 15—20 mm. in the presence of potassium hydroxide, it gives rise to cyclohexadiene, whilst 1:2-dibromocyclohexane furnishes  $\Delta^1$ :3-cyclohexadiene and chlorocyclopentane yields cyclopentene. F. M. G. M.

**Derivatives of Phenylacetylene, Methoxyphenylacetylene, and Allied Compounds.** FRANZ KUNCKELL [with KURT ERAS, EMIL MÜLLER, and ALFRED HILDEBRANDT] (*Ber. Dent. Pharm. Ges.*, 1913, 23, 188—227).—A recapitulation and extension of previous work on the preparation of derivatives of phenylacetylene from aryl chloromethyl ketones (A., 1897, i, 282, 522; 1901, i, 75, 552, 638; 1903, i, 413).

*p*-Tolylacetylene combines with bromine to form a dibromide, a pale yellow oil, b. p. 139—143°/13 mm.,  $D_{20}^{25}$  1.669, and a yellow, viscoid, oily tetrabromide; with ammoniacal silver nitrate it yields a white, gelatinous silver salt, which forms an explosive grey powder when dry. The copper salt is light yellow, and is oxidised by aqueous potassium ferricyanide in the presence of potassium hydroxide to di-*p*-tolylbutadiene,  $C_6H_4 \cdot C \equiv C : C \equiv C \cdot C_6H_4$ . This crystallises in white needles, m. p. 183°, and yields a dibromide, m. p. 148°, tetrabromide, m. p. 163°, and an octabromide, m. p. 156—157°.

*p*-Ethylphenylacetylene gives a yellow oily dibromide, b. p. 168—172°/20 mm.,  $D_{20}^{25}$  1.598, a tetrabromide, and greenish-grey silver salt; the copper salt forms a light yellow powder, and is oxidised by alcoholic potassium ferricyanide to di-*p*-ethylphenylbutadiene, white needles, m. p. 72°.

$\alpha\beta$ -Dichloro-2-bromo-5-methoxyphenylene,  $OMe \cdot C_6H_3Br \cdot CCl_2CHCl$ , prepared from 2-bromo-5-methoxyphenyl chloromethyl ketone and phosphorus pentachloride, forms a yellowish-brown oil, b. p. 210—215°. 25 mm.,  $D_{20}^{25}$  1.3610. When heated with phosphorus pentachloride on the water-bath, 3:4-dichloroacetyl-1-methoxybenzene gives rise to 1-methoxy-3:4-bis- $\alpha\beta$ -dichlorovinylbenzene,  $OMe \cdot C_6H_3(CCl_2CHCl)_2$ , a pale yellow liquid, b. p. 160—170°/47 mm.,  $D_{20}^{25}$  1.461; if the reaction is carried out at a higher temperature, 2:5-dichloro-1-methoxy-3:4-bis- $\alpha\beta$ -dichlorovinylbenzene,  $OMe \cdot C_6H_2(CCl_2CHCl)_2$ , a yellow oil, b. p. in vacuum 170—180°,  $D_{20}^{25}$  1.570, is produced.

$\alpha\beta$  2:5-Tetrachloro-4-methoxystyrene,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Cl}_4\cdot\text{CCl}\cdot\text{CHCl}$ , prepared by boiling *p*-methoxyphenyl chloromethyl ketone with excess of phosphorus pentachloride, is a yellow liquid of aromatic odour, b. p.  $165\text{--}175^\circ/18$  mm.,  $D^{17}_4$  1.44; the prolonged action of phosphorus pentachloride gives rise to  $\alpha\beta$  2:3:5-pentachloro-4-methoxystyrene, a yellow oil which has b. p.  $180\text{--}190^\circ/20$  mm.,  $D^{18}_4$  1.6160, and solidifies when kept.

$\alpha\beta$ -Dichloro-*p*-ethoxystyrene, prepared from *p*-ethoxyphenyl chloromethyl ketone, is a brownish-yellow liquid of disagreeable odour, b. p.  $170\text{--}180^\circ/26$  mm.,  $D^{20}_4$  1.243.

5-Methoxy-*o*-tolyl chloromethyl ketone gives rise to  $\alpha\beta$ -dichloro-5-methoxy-2-methylstyrene,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CCl}\cdot\text{CHCl}$ , a pale yellow oil, b. p.  $160^\circ/20$  mm.,  $D^{15}_4$  1.2520; chloro-5-methoxy-*o*-tolylacetylene has b. p.  $145\text{--}150^\circ/15$  mm.,  $D^{15}_4$  1.166. 5-Methoxy-*o*-tolylacetylene is a pale yellow liquid of ethereal odour, b. p.  $110\text{--}120^\circ/18$  mm.,  $D^{17}_4$  1.011.

2:4-Dimethoxyphenyl chloromethyl ketone, prepared from resorcinol dimethyl ether and chloroacetyl chloride, crystallises in yellow leaflets, m. p.  $104^\circ$ , and yields with phosphorus pentachloride,  $\alpha\beta$  dichloro-2:4-dimethoxystyrene, a reddish-yellow liquid which has a sweet odour and becomes crystalline when kept, b. p.  $160\text{--}165^\circ/18$  mm.

Resorcinol diethyl ether and chloroacetyl chloride yield 4:4-(*di*-chloroacetyl-1:3-diethoxybenzene,  $\text{C}_6\text{H}_2(\text{OEt})_2(\text{CO}\cdot\text{CH}_2\text{Cl})_2$ , small, yellow needles, m. p.  $108^\circ$ .

*Di*-*p*-chloroacetyldiphenyl ether,  $\text{O}(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Cl})_2$ , prepared from diphenyl ether and chloroacetyl chloride, forms greenish granules, m. p.  $111^\circ$ , and gives rise to *di*- $\alpha\beta$ -dichlorovinylldiphenyl ether,  $\text{O}(\text{C}_6\text{H}_4\cdot\text{CCl}\cdot\text{CHCl})_2$ , a viscid liquid having a green shimmer, b. p.  $225^\circ/20$  mm.

2:6-Dichloroacetylmesitylene, from chloroacetyl chloride and mesitylene, forms large, lustrous crystals, m. p.  $134\text{--}135^\circ$  (compare Meyer, A., 1897, i. 55), and yields 1:3:5-trimethyl-2:6-bis- $\alpha\beta$ -dichlorovinylbenzene,  $(\text{CHMe}_2(\text{CCl}\cdot\text{CHCl}))_2$ , a colourless oil, b. p.  $184\text{--}181^\circ/12$  mm.,  $D^{15}_4$  1.3106. When impure, the last-named substance gradually loses hydrogen chloride on exposure to air, yielding a white substance, m. p.  $95^\circ$ .

2:4:6-Triethylphenyl chloromethyl ketone, prepared from 2:4:6-triethylbenzene, is a strongly refractive liquid, b. p.  $207\text{--}215^\circ/20$  mm., and yields  $\alpha\beta$  dichloro-2:4:6-triethylstyrene, which forms a golden-yellow oil of aromatic odour, b. p.  $175\text{--}18$  mm.,  $D^{15}_4$  1.447; 2:4:6-triethylphenylchloroacetylene, a yellow oil, b. p.  $155^\circ/18$  mm.,  $D^{15}_4$  1.0236; 2:4:6-triethylphenylacetylene, a colourless liquid, b. p.  $124\text{--}126^\circ/14\text{--}16$  mm.,  $D^{21}_4$  0.9064, which forms a yellow, amorphous copper salt.

2:6-Dichloroacetyl-1:3:5-triethylbenzene,  $\text{C}_6\text{H}_3\text{Et}_3(\text{CO}\cdot\text{CH}_2\text{Cl})_2$ , crystallises in transparent, hexagonal plates, m. p.  $71\text{--}72^\circ$ , and gives rise to 1:3:5-triethyl-2:6-di- $\alpha\beta$ -dichlorovinylbenzene,  $\text{C}_6\text{H}_3\text{Et}_3(\text{CCl}\cdot\text{CHCl})_2$ , a golden-yellow oil, b. p.  $210\text{--}215^\circ/17\text{--}18$  mm.,  $D^{15}_4$  1.245.

2:4-Di-chloroacetyl-6-acetyl-1:3:5-triethylbenzene,  $\text{COMe}\cdot\text{C}_6\text{H}_3\text{Et}_3(\text{CO}\cdot\text{CH}_2\text{Cl})_2$ , from 2:4:6-triethylphenyl methyl ketone and chloroacetyl chloride, crystallises in stout, transparent needles, m. p.  $72^\circ$ . F. B.

Preparation of Sulphonic Acids of the Benzene and Naphthalene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 255724. Compare Friedländer and Lucht, A., 1894, i, 138).—When an electric current is passed through an alkaline solution of an anilino, naphthylamine- or naphthol-polysulphonic acid in the presence of sodium amalgam a sulphonic group is eliminated.

The reduction of the following compounds is described: aniline-3:6-disulphonic acid to aniline-3-sulphonic acid;  $\alpha$ -naphthylamine-4:8-disulphonic acid to  $\alpha$ -naphthylamine-4-sulphonic acid;  $\beta$ -naphthylamine-4:8-disulphonic acid to the corresponding -8-sulphonic acid;  $\beta$ -naphthylamine-5:7-disulphonic acid to  $\beta$ -naphthylamine-7-sulphonic acid;  $\alpha$ -naphthylamine-3:5:7-trisulphonic acid to  $\alpha$ -naphthylamine-3:7-disulphonic acid;  $\alpha$ -naphthylamine-2:4:6-trisulphonic acid to  $\alpha$ -naphthylamine-2:4-disulphonic acid;  $\alpha$ -naphthylamine-2:5:7-trisulphonic acid to  $\alpha$ -naphthylamine-2:7-disulphonic acid;  $\alpha$ -naphthol-3:8-disulphonic acid to  $\alpha$ -naphthol-3-sulphonic acid;  $\alpha$ -naphthol-2:4:8-trisulphonic acid to  $\alpha$ -naphthol-2:1-disulphonic acid, and  $\beta$ -naphthol-3:6:8-trisulphonic acid to  $\beta$ -naphthol-3:6-disulphonic acid.

F. M. G. M.

$\Delta^1$ -Dihydronaphthalene. FRITZ STRAUS (*Ber.*, 1913, 46, 1051—1055).—By the exhaustive methylation of tetrahydro- $\beta$ -naphthylamine, Willstätter and King (this vol., i, 353) have obtained a dihydronaphthalene which they consider to be identical with the  $\Delta^2$ -dihydronaphthalene, described by Bamberger (A., 1896, i, 99).

The author points out, however, that the properties of Willstätter and King's dihydro-compound show such complete agreement with those of the  $\Delta^1$ -dihydronaphthalene (this vol., i, 256) that there can be no doubt as to the identity of the two hydrocarbons.

$\Delta^2$ -Dihydronaphthalene forms a dibromide differing very little in m. p. from that of the  $\Delta^1$ -isomeride. The removal of bromine by means of zinc in alcoholic solution yields in each case the original hydrocarbon. The statement of Willstätter and King that their dihydronaphthalene can be obtained by the removal of bromine from the dibromide of Bamberger's  $\Delta^2$ -dihydro-compound is, therefore, erroneous.

F. B.

Halogen Compounds of Anthracene. KURT H. MEYER and KURT ZAHN (*Annalen*, 1913, 396, 166—180).—The halogen additive compounds of anthracene are derivatives of 1:2:3:4-tetrahydroanthracene. Attempts to replace the halogen atoms by hydroxyl, amino, and other groups have been unsuccessful, but a new case of isomerism has been observed.

Gaube and Liebermann have shown that the action of bromine vapour on anthracene yields 9:10-dibromoanthracene tetrabromide. This yields 1:3:9:10-tetrabromoanthracene by treatment with alcoholic potassium hydroxide, 2:9:10-tribromoanthracene by heating, and 9:10-dibromoanthracene by reduction with zinc and acetic acid.

By treating anthracene moistened with chloroform with bromine (4 mols.) in chloroform, a substance,  $C_{14}H_8Br_4$ , m. p. 134–135° (decomp.), colourless needles, is obtained, which reacts like the older isomeride towards alcoholic potassium hydroxide, heating, and reducing agents. The two isomerides, therefore, are structurally alike. It is suggested that the two are stereoisomeric, the new compound, which is called *α-9:10-dibromoanthracene tetrabromide*, having the four homonuclear bromine atoms in *cis* positions, whilst in the older (*β*;) compound they are alternately *cis* and *trans*. These configurations are in harmony with a property which is characteristic of the *α*-, but not of the *β*-isomeride. *α-9:10-Dibromoanthracene tetrabromide* in boiling benzene is decomposed into bromine and 9:10-dibromoanthracene by exposure to sunlight or to the light of a mercury lamp; the change is not reversible in boiling benzene in darkness.

*α-9:10-Dichloroanthracene tetrabromide*,  $C_{14}H_8Cl_2Br_4$ , m. p. 141–142° (decomp.), colourless, hexagonal prisms, prepared from dichloroanthracene and bromine (2 mols.) in chloroform, exhibits a similar photochemical decomposition in benzene, whilst the long-known *β*-isomeride does not.

The 9:10-dichloroanthracene tetrachloride obtained by Hammerschlag by passing chlorine into a benzene solution of anthracene is the *β*-isomeride, since it is photochemically inactive and does not liberate iodine from potassium iodide. The *α*-isomeride has not been obtained. The *β*-isomeride yields 1:3:9:10-tetrachloroanthracene (the constitution of which is proved by its conversion into 1:3-dichloroanthraquinone) by treatment with alcoholic potassium hydroxide, 2:3:9:10-tetrachloroanthracene, m. p. 240–241°, yellow needles (yielding 2:3-dichloroanthraquinone by oxidation), by heating above its m. p., and 9:10-dichloroanthracene by reduction with zinc and acetic acid.

9:9:10:10-Tetrachloroanthracene, m. p. 170° (Schwarzer gives 149–150°), obtained together with 9:10-dichloroanthracene tetrachloride by passing chlorine into a chloroform solution of anthracene at 0°, yields the *dianil*,  $NPh:C\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle:C:NPh$ , m. p. 201–202°, golden-yellow leaflets, with aniline in boiling alcohol, and the *tetra-methylacetal*,  $C(OMe)_2\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle C(OMe)_2$ , m. p. 161–162°, colourless crystals, with boiling methyl alcohol and sodium carbonate. (C. S.)

Preparation of *o*-Substituted Derivatives of Acetoacetanilide and Their Homologues. FARBENTAFERKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 256621).—3-Chloroacetoaceto-*o*-toluidide, colourless needles, m. p. 120°, is obtained in 66% yield when a solution of ethyl acetoacetate in chlorobenzene is added to a hot solution of 3-chloro-*o*-toluidine in the same solvent.

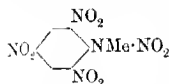
*o*-Chloroacetoacetanilide is prepared in 75% yield in a similar manner from *o*-chloroaniline.

*Acetoaceto-o-aniside*, a colourless, crystalline powder, has m. p. 84,

whilst the analogous compounds from 3-amino-*p*-tolyl ethyl ether and from phenyl *o*-aminophenyl ether have m. p. 80° and 61° respectively.

F. M. G. M.

**The Manufacture of Tetranitromethylaniline.** F. LANGENSCHIEDT (*Zeitsch. ges. Schiess-Sprengstoffwesen*, 1912, 7, 445—447).—2:4:6-N-Tetranitromethylaniline ("Tetrit") (annexed formula), m. p. 129—130°,



is obtained in 87% yield when pure methyl- or dimethyl-aniline is dissolved in 10 parts of concentrated sulphuric acid (pure and free from lead), thoroughly cooled, and slowly added to 4·3 parts of nitric acid (47° Be) at 40°, 44° being the utmost limit to which the temperature may rise in the early stages of the operation; later, when the violence of the action decreases, it is allowed to rise to, and maintained at, about 53—55°, and after about eleven hours the nitration is completed. The product is purified by crystallisation from benzene.

F. M. G. M.

[Preparation of 4-Chloro-2:6-diaminophenol.] FARBWERKE FORM. MEISTER, LUCIUS & BRUNING (D.R.P. 256794).—4-Chloro-2:6-diaminophenol, obtained by the reduction of 4-chloro-2:6-dinitrophenol, crystallises from hot water in needles, has m. p. 88—89°, and furnishes crystalline salts.

3:5-Diamino-*p*-cresol, m. p. 146°, is prepared by the reduction of the corresponding 3:5-dinitro-*p*-cresol.

F. M. G. M.

**Preparation of Dialkylaminoformic Esters.** FARBENFABRIKEN FORM. FRIEDR. BAYER & Co. (D.R.P. 255942).—When halogen formic esters are treated with trialkylamines the following reaction takes place:  $\text{ClCO}_2\text{R} + \text{NMe}_3 = \text{NMe}_3\text{Cl} \cdot \text{CO}_2\text{R}$ , and the compounds so obtained when heated give rise to dialkylaminoformic esters of the general formula:  $\text{NMe}_2\text{Cl} \cdot \text{CO}_2\text{R} = \text{NMe}_2 \cdot \text{CO}_2\text{R} + \text{MeCl}$  (R may be alkyl, aryl, or alkylaryl).

Phenyl dimethylaminoformate,  $\text{NMe}_2 \cdot \text{CO}_2\text{Ph}$ , colourless needles, m. p. 44—45°, b. p. 134—135°/16 mm., is obtained in quantitative yield when a cooled benzene solution of trimethylamine is slowly treated with phenyl chloroformate; the intermediate compound,  $\text{NMe}_3\text{Cl} \cdot \text{CO}_2\text{Ph}$ , separates as a colourless, crystalline precipitate, and, on subsequently boiling, the reaction mixture is slowly converted into the foregoing ester.

Tolyl dimethylaminoformate,  $\text{NMe}_2 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , a viscid, colourless oil, b. p. 145—195°/15 mm., consisting of a mixture of the ortho-, meta-, and para-isomerides, is prepared in a similar manner from the mixture of tolyl chloroformates, b. p. 85—105°/18 mm., obtained by the action of carbonyl chloride on a freshly distilled benzene solution of crude cresol (b. p. 190—206°) in the presence of dimethylaniline.

$\beta$ -Naphthyl chloroformate, colourless prisms, m. p. 57° (prepared from carbonyl chloride and  $\beta$ -naphthol), when treated with trimethylamine furnishes the compound,  $\text{NMe}_3\text{Cl} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_7$ , as a colourless, crystalline precipitate, and on boiling is converted into  $\beta$ -naphthyl dimethylaminoformate,  $\text{NMe}_2 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_7$ , colourless crystals, m. p. 92°.



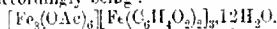
iso. *myl dimethylaminoformate*,  $\text{Me}_2\text{N}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_{11}$ , a colourless oil, b. p. 194—197°, and *phenyl diethylaminoformate*,  $\text{NEt}_2\cdot\text{CO}_2\text{Ph}$ , a colourless oil, b. p. 142—146°/13 mm, are prepared in a similar manner.

F. M. G. M.

**Preparation of Aromatic Selenocyno-compounds.** FARNWERKE VORM. MEISTER, LECIUS & BRÜNING (D.R.P. 255982).—An account of the preparation of compounds previously described by Bauer (this vol., i, 263); the m. p. of *o*-nitrophenyl selenocyanate is given as 144—145° (*loc. cit.*, 142°).

F. M. G. M.

**Iron Compounds of Phenols. IV.** RUDOLF F. WEINLAND and KARL BINDER (*Ber.*, 1913, 46, 874—885).—The dark blue substance obtainable from catechol and ferric acetate, which dissolves in water to a green solution, was provisionally regarded as having the structure  $\text{Fe}_3(\text{C}_6\text{H}_3\text{O}_2)_2\cdot\text{OH}\cdot 7\text{H}_2\text{O}$  (A., 1912, i, 445), but it is now shown to yield acetic acid when warmed, and to contain actually one atomic weight of iron to a molecular weight of acetic acid and of catechol; it is obtained when two molecular proportions of ferric acetate are mixed with 1—2 of catechol in aqueous solution. If, however, four times the above quantity of catechol is used the violet acid,  $\Pi \left[ \text{Fe}(\text{C}_6\text{H}_3\text{O}_2)_2 \right] \cdot \text{H}_2\text{O}$  (*loc. cit.*), is obtained. It is therefore a probable conclusion that the substance which yields a green solution is a complex salt containing as components the above violet acid and the hexa-acetotriferric base (Weinland and Gussmann, A., 1910, i, 457), the constitution accordingly being:



The view is confirmed by the production of a green colour on the addition of the red solution of ferric acetate to a solution of an alkali salt of the above violet acid, or on the addition of a little catechol to ferric acetate solution. It is suggested that the green coloration produced by ferric chloride solution with catechol may be due to the formation of some analogous complex salt. The green colour of the solutions of the above complex salt is not due to the mere superposition of the colours of the acid and metallic radicles, but the possibility is not excluded that some decomposition may occur during the process of solution with formation of still unknown complexes.

The preparation of the violet acid can be effected without the addition of sodium acetate (compare A., 1912, i, 445), provided that sufficient catechol is added to decompose all the ferric acetate.

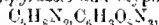
As ferric chloride is soluble in certain organic solvents, the reaction of this substance with catechol was examined in other solvents than water. In ethereal solution the reaction product was a crystalline, blackish-brown substance,  $\text{Fe}(\text{O}\cdot\text{C}_6\text{H}_3\text{O}_2)_2\cdot\text{OH}\cdot\text{Cl}_3\cdot\text{Et}_2\text{O}$  (compare A., 1912, i, 850), which may possibly be an oxonium salt of ether with the acidic portion of the substance; it is very sensitive to moisture, and soon becomes decomposed in the air; in alcohol it gives a blue solution. The reaction in acetophenone solution yields a product which when precipitated by pyridine forms bluish-black, microscopic leaflets of a

substance which may be regarded as a pyridino salt of the acid present in the last substance, that is,  $(C_5H_5N)_3[4Fe(C_6H_4O_2Cl_2)_4]$ . In pyridine solution a bluish-black, crystalline powder consisting of microscopic leaflets is obtained; the structure of this substance may be that of a salt of the red acid,  $H_3[Fe^{III}(C_6H_4O_2)_3]$  (A., 1912, i, 445), with complex bases, and the formula  $Fe(C_6H_4O_2)_3 \leftarrow [Fe(C_5H_5N)_3Cl_2, H_2O]$  is suggested.

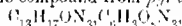
The potassium salt of the violet acid retains its molecule of water in a vacuum over sulphuric acid for six months, and the potassium salt of the red acid holds its  $2H_2O$  equally tenaciously; the sodium salt of the latter acid, however, yields 8 of its 9  $H_2O$  under similar treatment.

D. F. T.

**Some Additive Products of Styphnic Acid.** CLAUDIO AGOSTINELLI (*Gazzetta*, 1913, 43, i, 124—128).—The additive compound of 3:5-dimethylpyrazole and styphnic acid,

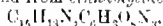


crystallises in golden-yellow scales, m. p. 203—204°. The compound from antipyrine,  $C_{11}H_{12}ON \cdot C_6H_3O_5N_3$ , crystallises in canary-yellow laminae, m. p. 204°. The compound from pyrazidone,



forms thin, yellow needles, m. p. 191°. The compound from camphorphenylhydrazine,  $C_{19}H_{16}N \cdot NHPb \cdot C_6H_3O_5N_3$ , crystallises in green, woolly needles, m. p. 150—151°. The compound from acetonephenylhydrazine,  $C_8H_{10}N \cdot NHPb \cdot C_6H_3O_5N_3$ , crystallises in yellowish-green scales, m. p. 104—106°.

The compound from cinnamaldehydephenylhydrazine,  $C_{19}H_{14}N_2 \cdot (C_6H_3O_5N_3)_2$ , forms micute, pale green needles, m. p. 137—138°. The compound from benzylidenemalline,  $C_{13}H_{11}N \cdot C_6H_3O_5N_3$ , crystallises in pale yellow scales, m. p. 193°. The compound from cinnamylidenemalline,

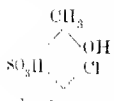


crystallises in bright red laminae, m. p. 178°. The compound from benzylidenemazine,  $C_{14}H_{12}N_2 \cdot C_6H_3O_5N_3$ , forms yellow needles, m. p. 152°. The compound from cinnamylidenemazine,  $C_{17}H_{16}N_2 \cdot C_6H_3O_5N_3$ , crystallises in orange-yellow needles, m. p. 176°.

R. V. S.

**Preparation of 2:3-Dihydroxytoluene.** SACCHARIN-FABRIK ANTIENGESELLSCHAFT VORM. FAHLBERG, LISF & CO. (D.R.-P. 256345).—2:3-Dihydroxytoluene, m. p. 68°, b. p. 211° or 112–3 mm., is obtained by Limpach (A., 1892, 447) but m. p. 47°, and the following method of preparation is now described. *o*-Cresol is sulphated, and the *o*-cresol-5-sulphonic acid so obtained, chlorinated, when it yields 3-chloro-*o*-cresol-5-sulphonic acid (annexed formula); this when

heated at 130° with dilute sulphuric acid gives rise to 3-chloro-*o*-cresol, m. p. 185°, or if fused for 8–10 hours at 160–170° subsequently heated at 200° with water under pressure, it yields 2:3-dihydroxytoluene in glistering, colourless leaflets.



P. M. G. M.

Some New Polymerides of the Phenols with Propenylic Side-chains. ERNESTO PUXEDDU (*Gazzetta*, 1913, 43, i, 128—133).—The author has obtained new polymerides of isosafrole and anethole by methods based on the employment of an anhydrous ethereal solution of ferric chloride.

When an anhydrous ethereal solution of isoeugenol and ferric chloride is treated with dry hydrogen chloride for three hours, the diisoeugenol already known is produced.

If an absolute ethereal solution of isosafrole and ferric chloride is treated with dry hydrogen chloride for five days, a new polymeride of isosafrole is produced; it crystallises in spherical nodules, m. p. 92°, and reacts with bromine with evolution of hydrogen bromide and formation of an oily product.

Anethole, when treated in a manner similar to that described in the two preceding cases, yields a new polymeride, which, however, is better prepared by simply mixing anhydrous ethereal solutions of anethole and ferric chloride; the mixture deposits a white powder, which does not melt at 340°.

R. V. S.

Action of Nitrous Acid on Ethylisoeugenol. ERNESTO PUXEDDU (*Gazzetta*, 1913, 43, i, 133—138. Compare A., 1912, i, 186).—The paper deals with the ethylisoeugenol peroxide previously described (*loc. cit.*) with a view to showing its analogy to similar substances investigated by Angeli and others (A., 1893, i, 261, 263; 1894, i, 72; 1895, i, 35). When the peroxide is boiled with alcoholic potassium hydroxide for a few minutes, it is converted into a substance,  $C_{12}H_{14}O_4N_2$ , which crystallises in long, yellow, prismatic needles, which become red at 170°, m. p. 180° (decomp.).

Reduction of the peroxide with tin and hydrochloric acid yields a furazan derivative,  $C_{12}H_{14}O_3N_2$ , m. p. 116°. When the reduction is effected by zinc and acetic acid in certain conditions, ethylisoeugenol  $\alpha$ -dioxime,  $C_{12}H_{16}O_3N_2$ , is produced; it forms lustrous scales, m. p. 159°. On heating at 150° for some hours, it yields the  $\beta$ -dioxime, which forms prismatic crystals, m. p. about 190°.

R. V. S.

Some Derivatives of Hydroxyquinol. IX. GUIDO BARGELLINI (*Gazzetta*, 1913, 43, i, 164—175. Compare Bargellini and Avrunth, A., 1911, i, 68).—The paper deals with the constitution of two substances obtained by the action of zinc chloride on triacetylhydroxyquinol, and described in the paper cited.

The red substance of m. p. 200—202° is 2:4:5-trihydroxyacetophenone, for it is formed by the saponification of the white substance of m. p. 165—166°, and it also results from the action of potassium persulphate on resacetophenone in alkaline solution (compare Bargellini and Aureli, A., 1911, i, 855). Benzoyl chloride yields 2:4:5-tribenzoyloxyacetophenone with both substances; it forms colourless needles, m. p. 131—133°. Acetyl chloride gives with both red and white compounds a substance of the empirical formula  $C_{21}H_{20}O$ , m. p. 110—111°, which is 2:4:5-triacetoxyacetophenone. Both red and white compounds yield diacetyl- $\beta$ -methylasculetin (Bargellini and Monteghini, A., 1912, i, 292) when heated with acetic anhydride and

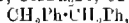
sodium acetate; the formation of another substance, which begins to decompose at  $245^{\circ}$ , was also observed. The reactions above described, taken in conjunction with the results of the molecular weight determination and of the estimation of saponifiable acetic acid in the compound, show that the white substance is a *hydroxydiacetoxy-arelophenane*.

The reaction between zinc chloride and triacetylhydroxyquinol thus results in a migration of one of the acetyl groups to a carbon atom of the nucleus. Other similar reactions are known. R. V. S.

**Behaviour of Individual Organo-magnesium Compounds Towards Aromatic Ethers.** VLADIMIR V. TSCHELINCEV and B. V. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 289–309. Compare A., 1906, ii, 334, 335; A., 1907, i, 499; A., 1908, i, 254; Stadnikov, and also Stadnikov and Kuzmina-Aron. A., 1912, i, 971).

—The authors have investigated the products formed and the thermal changes involved in the action of magnesium propyl iodide on (1) benzyl ethyl ether; (2) diphenylmethyl ethyl ether; and (3) triphenylmethyl ethyl ether. The products are (1) phenylbutane, diphenylmethane, benzene, and ethyl alcohol; (2) diphenylbutane and tetraphenylethane, and (3) triphenylmethane and ethyl alcohol. The heat effects observed also indicate, not merely a combination of the ether with the organo-magnesium compound, but a more profound interaction.

These results show that when ethers of the aromatic series, which are less stable than the corresponding ones of the aliphatic series, react with organo-magnesium compounds, they are partly divided at the junction of the aromatic radicle with the oxygen of the alkoxy-group. This division leads to the formation of aromatic hydrocarbons of two types: (1)  $\text{CH}_2\text{PhPr}$ ,  $\text{CHPh}_2\text{Pr}$ ,  $\text{CPh}_3\text{Pr}$ , and (2)



$\text{CHPh}_2\cdot\text{CHPh}_2$ ,  $\text{CPh}_3\cdot\text{CPh}_3$ . These hydrocarbons are produced in accordance with the scheme advanced by Erlenmeyer, jun.: (1)  $\text{R}\cdot\text{OEt} + \text{IMg}\cdot\text{Pr} = \text{R}\cdot\text{Pr} + \text{OEt}\cdot\text{MgI}$ , and (2)  $2\text{R}\cdot\text{OEt} + 2\text{IMg}\cdot\text{Pr} = \text{R}\cdot\text{R} + \text{Pr}\cdot\text{Pr} + 2\text{OEt}\cdot\text{MgI}$ .

Since these hydrocarbons represent the actual products of the interaction of organo-magnesium compounds and ethers, and are not formed only after the action of water on these products, any attempt to draw conclusions concerning the structure of the ethereal complexes of organo-magnesium compounds on the basis of experimental results of this kind is pure speculation.

Further, no certain conclusions can be deduced from consideration of the products obtained by decomposition of the complexes by means of carbon dioxide (compare Stadnikov and Kuzmina-Aron, A., 1912, i, 971). Since such decomposition is not quantitative, especially when molecular proportions of the ether and organo-magnesium compound are taken, and at the same time there is no exclusion of the possibility of formation from undecomposed magnesium alkyl iodide of the corresponding fatty acid, and hence of, for example, triphenylacetic acid.

In deciding between the two structures:  $R_3O(MgR)I$  and  $R_3O(MgI)R$ ,

it must be borne in mind that ethereal complexes of this type are obtained, not only with such compounds as  $MgRI$ , but also with magnesium iodide, and in the latter case the only possible structure is  $R_3OI \cdot Mg \cdot OIR$ . T. H. P.

#### Reduction by means of Organo-magnesium Compounds

ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 163—166).—The author has previously (*A.*, 1912, i, 622) expressed the opinion that the formation of triphenylmethane by the interaction of triphenyl methyl ethyl ether, propyl iodide, and magnesium in an indifferent solvent is due to hydrolytic decomposition of the ether into triphenyl methyl iodide and reduction of the latter to the corresponding hydrocarbon. As alkyl iodides and magnesium, however, react in absence of an ether or other catalyst, it may be that in the above case no etherate of the type  $Pr \cdot Mg \cdot OEt$  is formed, but that these reactions take place between the individual organo-magnesium compounds and the ether.

In order to test the accuracy of this view, experiments were made in which the triphenylmethyl ethyl ether was replaced by other oxygenated compounds, such as ketones. The reaction between  $\beta$ -benzopinacolin and magnesium propyl iodide in toluene solution proceeds in the same direction as the reaction with triphenylmethyl in presence of ethyl ether, giving a compound apparently identical with benzopinacolin alcohol. Similarly, benzophenone yields benzhydrol and other compounds. It is known that the action of organo-zinc compounds on aldehydes and on ketones may, under certain experimental conditions and with certain radicals in the organo-metallic compounds, result in the reduction of the aldehydes to primary, and of the ketones to secondary, alcohols; hence the reaction with  $\beta$ -benzopinacolin may be represented by the equation:  $CPh_3 \cdot COPh + MgPrI = CPh_3 \cdot CHPh \cdot OMgI + C_3H_8$ .

That the reaction between nascent organo-magnesium compounds and ketones is not generally limited to such a reduction is, however, rendered evident by the fact that the secondary alcohol is not the sole final product.

These considerations indicate the possibility that the reaction between triphenylmethyl ethyl ether and magnesium propyl iodide may be one of direct reduction, without intermediate formation of iodide:  $CPh_3 \cdot OEt + MgPrI = CHPh_3 + OEt \cdot MgI + C_3H_8$ . T. H. P.

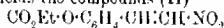
Phenylethanolamines, Phenylnitroethanols, and their Hydroxy derivatives. KARL W. ROSENMUND (*Ber.*, 1913, 46, 1031—1050, Compare *A.*, 1910, i, 106; 1911, i, 34).—An account of a preparation of a number of  $\beta$  hydroxy- $\beta$  arylethylamines,  $OH \cdot CHR \cdot CH_2 \cdot NH_2$ , by the reduction of the corresponding nitro-alcohols,  $OH \cdot CH \cdot CHR \cdot CH_2 \cdot NO_2$ . The latter compounds are obtained in good yield by decomposing the sodium salts, produced by the condensation of aromatic aldehydes with nitromethane in the presence of sodium methoxide, with acetic acid. On treatment with mineral acids or when heated, the nitro-alcohol

lose water with the formation of the corresponding nitrostyrenes,  $R\cdot CH:CH\cdot NO_2$ . They dissolve in alkalis, yielding colourless solutions from which acetic acid liberates the nitro-alcohols unchanged, whilst mineral acids give rise to  $\beta$ -nitrostyrenes.

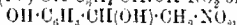
When dissolved in alkalis and the solutions acidified with acetic acid, the  $\beta$ -nitrostyrenes combine with water to form nitro-alcohols.

A similar addition of alcohol, resulting in the formation of nitro-ethers of the type  $OEt\cdot CHR\cdot CH_2\cdot NO_2$ , may be effected by treating the nitrostyrenes with alcoholic alkali hydroxides and subsequently acidifying with acetic acid.

Although hydroxybenzaldehydes do not directly condense with nitromethane, the preparation of the corresponding nitrostyrenes and nitro-alcohols may be readily accomplished by the method illustrated in the following example: *p*-hydroxybenzaldehyde is converted into *p*-ethylcarbonatobenzaldehyde (I),  $CO_2Et\cdot O\cdot C_6H_4\cdot CHO$ , which instantly reacts with nitromethane in the presence of alkali, yielding the salt  $CO_2Et\cdot O\cdot C_6H_4\cdot CH(OH)\cdot CH\cdot NO_2\cdot OK$ ; on treatment with hydrochloric or acetic acid this yields the compounds (II)



and (III)  $CO_2Et\cdot O\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NO_2$ , respectively. If excess of alkali is employed and the reaction mixture allowed to remain for one to two minutes, the carbethoxy-group is removed and subsequent acidification yields (IV)  $OH\cdot C_6H_4\cdot CH\cdot CH\cdot NO_2$  or (V)

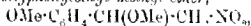


accordingly as hydrochloric or acetic acid is employed.

$\beta$ -Nitro- $\alpha$ -phenylethyl alcohol,  $OH\cdot CHPh\cdot CH_2\cdot NO_2$ , prepared by condensing benzaldehyde with nitromethane in alcoholic solution by means of sodium methoxide below  $8^\circ$  and acidifying the aqueous solution of the resulting sodium salt with dilute acetic acid, is a yellow oil, b. p.  $163-165/15$  mm. On treatment with sodium methoxide in methylalcoholic solution,  $\beta$ -nitrostyrene yields a colourless solution, from which the successive addition of acetic acid and water liberates  $\beta$ -nitro- $\alpha$ -phenylethyl methyl ether,  $OMe\cdot CHPh\cdot CH_2\cdot NO_2$ , as a pale yellow oil, b. p.  $140-141/15$  mm.

$\beta$ -Nitro- $\alpha$ -*p*-methoxyphenylethyl alcohol,  $OMe\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NO_2$ , prepared by acidifying with acetic acid an aqueous solution of the sodium salt, obtained by the condensation of anisaldehyde and nitromethane with sodium methoxide, is a yellow oil, which partly decomposes on distillation or on treatment with mineral acids into  $\beta$ -nitro-*p*-methoxystyrene.

$\beta$ -Nitro- $\alpha$ -*p*-methoxyphenylethyl methyl ether,



is a yellow oil.

*p*-Benzoyloxybenzaldehyde condenses with nitromethane, yielding  $\beta$ -nitro-*p*-benzyloxystyrene,  $C_6H_5\cdot O\cdot C_6H_4\cdot CH\cdot CH\cdot NO_2$ , m. p.  $129^\circ$ , from which  $\beta$ -nitro- $\alpha$ -*p*-benzyloxyphenylethyl methyl ether,



m. p.  $105-106^\circ$ , is obtained in the usual manner.

*p*-Benzoyloxybenzaldehyde, prepared by the successive addition of the theoretical amount of potassium hydroxide and benzoyl chloride to an alcoholic solution of *p*-hydroxybenzaldehyde, yields with nitromethane

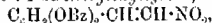
*β*-nitro-*p*-benzoyloxystyrene, which crystallises in slender, pale yellow needles, m. p. 153—155°. *β*-Nitro-*a*-*p*-benzoyloxyphenylethyl alcohol forms almost white, lustrous scales, m. p. 127—130°, and yields a white sodium salt. *p*-Ethylcarbonatobenzaldehyde (I), prepared from *p*-hydroxybenzaldehyde and ethyl chloroformate in the presence of alkali, is a colourless oil, b. p. 170—172°/13 mm., and yields *β*-nitro-*p*-ethylcarbonatostyrene (II), crystallising in slender, pale yellow needles, m. p. 112—113°.

*β*-Nitro-*a*-*p*-ethylcarbonatophenylethyl alcohol (III) forms yellow needles, m. p. 91.5°. *β*-Nitro-*p*-hydroxystyrene (IV), prepared by hydrolysing its acyl derivatives with cold aqueous potassium hydroxide, crystallises in stout, long needles, m. p. 154—160° (decomp.). *β*-Nitro-*a*-*p*-hydroxyphenylethyl alcohol (V) is a yellow syrup.

4-Benzoyloxy-3-methoxybenzaldehyde, prepared by benzoylating vanillin by the pyridine method, has m. p. 75–76°, and condenses with nitromethane, yielding *β*-nitro-4-benzoyloxy-3-methoxystyrene, which forms slender, pale yellow needles, m. p. 152—155°, and is hydrolysed by alcoholic potassium hydroxide to vanillylidene nitromethane (A., 1905, i, 65).

4-Ethylcarbonato-3-methoxybenzaldehyde, prepared from vanillin and ethyl chloroformate, has m. p. 71° and loses CO<sub>2</sub> at 135°, yielding 3-methoxy-4-ethoxybenzaldehyde; with nitromethane it yields *β*-nitro-4-ethylcarbonato-3-methoxystyrene, m. p. 125°, and *β*-nitro-*a*-4-ethylcarbonato-3-methoxyphenylethyl alcohol, which crystallises in stout needles, m. p. 84—86°.

3:4-Dibenzoyloxybenzaldehyde, prepared from protocatechualdehyde in a similar manner to that given for *p*-benzoyloxybenzaldehyde, separates from alcohol in rosettes of white needles, m. p. 96—97°, and gives rise to *β*-nitro-3:4-dibenzoyloxystyrene,



which forms slender, pale yellow needles, m. p. 143—144°, and is hydrolysed by alcoholic potassium hydroxide to *β*-nitro-3:4-dihydroxystyrene, crystallising in yellow needles or leaflets, m. p. 155—157°, with previous darkening at 145—148° (decomp. 160°).

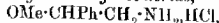
3:4-Diethylcarbonatobenzaldehyde, obtained from ethyl chloroformate and protocatechualdehyde, is a colourless oil, b. p. 215—217°/13 mm., and yields with nitromethane, *β*-nitro-3:4-diethylcarbonatostyrene, yellow needles, m. p. 72°.

Acidification of the products, resulting from the condensation of 3:4-diethylcarbonato- and 3:4-dibenzoyloxybenzaldehyde with nitromethane in the presence of sodium methoxide, with acetic acid yields *β*-nitro-*a*-3:4-diethylcarbonatophenylethyl alcohol and *β*-nitro-3:4-dibenzoyloxyphenylethyl alcohol, as yellow oils. If excess of sodium methoxide is used, *β*-nitro-3:4-dihydroxyphenylethyl alcohol is formed. Alkyl ethers of the last-mentioned compound have also been prepared, but these resemble the previously-mentioned nitro-alcohols derived from 3:4-dihydroxybenzaldehyde in being too unstable to allow of their isolation in a state of purity. Their constitution was therefore established by reduction to the corresponding amino-alcohols and ethers.

*β*-Hydroxy *β*-phenylethylamine is obtained by reducing *β*-nitro-*a*-

phenylethyl alcohol with sodium amalgam and acetic acid in aqueous alcoholic solution; it is accompanied by a substance of feeble basic properties, m. p. 217—218°.

*β-Methoxy-β-phenylethylamine hydrochloride*,



obtained by reduction of *β*-nitro-*α*-phenylethyl methyl ether in a similar manner, crystallises in white needles, m. p. 158—159°.

Successive treatment of *β*-nitro-*p*-methoxystyrene with alcoholic potassium hydroxide and acetic acid gives rise to *β*-nitro-*α*-*p*-methoxyphenylethyl ethyl ether. On reduction this yields *β*-ethoxy-*β*-*p*-methoxyphenylethylamine,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OEt}) \cdot \text{CH}_2 \cdot \text{NH}_2$ , as a syrup which slowly crystallises and yields a hydrochloride, m. p. 173—175° (decomp. 182°).

*β*-Methoxy-*β*-*p*-methoxyphenylethylamine, obtained from *β*-nitro-*α*-*p*-methoxyphenylethyl methyl ether, forms a hydrochloride, crystallising in white needles, m. p. 166—166.5° (decomp. 186—187°).

*β*-Hydroxy-*β*-*p*-methoxyphenylethylamine hydrochloride has m. p. 171—172°.

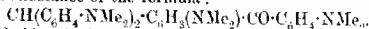
*β*-Nitro-*β*-3:4-dimethoxyphenylethyl methyl ether, obtained as a yellow oil by dissolving *β*-nitro-3:4-dimethoxystyrene (A., 1911, i, 34) in methyl-alcoholic sodium methoxide, is reduced by sodium amalgam and acetic acid to *β*-methoxy-*β*-3:4-dimethoxyphenylethylamine, identical with the arterenol trimethyl ether of Mannich and Neumann (A., 1910, i, 413).

The condensation of veratraldehyde and nitromethane with sodium methoxide yields the sodium salt of *β*-nitro-*α*-3:4-dimethoxyphenylethyl alcohol, which on decomposition with acetic acid and subsequent reduction is converted into *β*-hydroxy-*β*-3:4-dimethoxyphenylethylamine,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NH}_2$ , the hydrochloride of which crystallises in leaflets, m. p. 163°.

*β*-Hydroxy-3:4-dihydroxyphenylethylamine is obtained in an impure condition by the reduction of *β*-nitro-*α*-3:4-dihydroxyphenylethyl alcohol; the hydrochloride gives an intense catechol reaction with ferric chloride.

F. B.

**Action of Sulphuric Acid on Tetramethyldiaminobenzhydrol.** The Pinacone of Michler's Ketone. S. FISCHL (*Monatsh.*, 1913, 34, 337—350).—The observation of Rosenstiehl (A., 1895, i, 541) and of Weil (A., 1894, i, 419; 1895, ii, 145), that tetramethyldiaminobenzhydrol is converted into hexamethyltriaminotriphenylmethane by warming with dilute sulphuric acid is confirmed, and it is further shown that by the action of sulphuric acid, Michler's ketone is formed, which then condenses with some of the unchanged hydrol producing a substance of the formula:

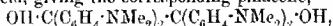


Tetramethyldiaminobenzhydrol, when dissolved in sulphuric acid and gently warmed, furnishes Michler's ketone (tetramethyldiaminobenzophenone), together with a substance,  $\text{C}_{24}\text{H}_{18}\text{ON}_4$ , m. p. 212—213°, crystallising from methyl alcohol in slender, silky needles, or from benzene on addition of light petroleum in short colourless prisms; it is readily soluble in benzene, less so in acetone, and must have the



constitution given above, since it is also formed by the condensation of Michler's ketone with tetramethyldiaminobenzhydrol in presence of sulphuric acid. It is unaffected by acids or alkalis, but on oxidation furnishes a greenish-blue dye. The reactions of the substance indicate that the  $\cdot\text{CO}\cdot$  group is in the ortho-position to the methane residue.

Tetramethyldiaminobenzophenone is not affected by zinc and acetic acid, but may be reduced electrolytically or by zinc with sulphuric or hydrochloric acid, giving the corresponding pinacone,



m. p.  $195^\circ$  (compare Escherich and Moest, A., 1903, i, 89). This is somewhat soluble in benzene, but almost insoluble in alcohol; its solution in acetic acid is colourless in the cold, but becomes blue on warming. It dissolves in sulphuric acid, forming a deep red solution, which on heating at  $115\text{--}120^\circ$  gives rise to the corresponding *pinacol*,

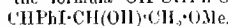


m. p.  $232\text{--}233^\circ$ , which crystallises with one mol. of benzene in glandular masses of glancing prisms. On heating with alcoholic potassium hydroxide, the pinacone is converted into a mixture of the ketone and the hydrol.

T. A. H.

**1:1-Dimethylolcyclobutane.** NICOLAI D. ZELINSKI and M. N. UDEMINOV (*Ber.*, 1913, 46, 1093—1094).—A solution of ethyltetramethylenedicarboxylate in absolute alcohol was added to sodium covered with dry ether, and, after the first vigorous action had subsided, the product was heated at  $130\text{--}140^\circ$  until the sodium was completely dissolved. After addition of water, the alcohol was removed by distillation and the residue poured into water and saturated with potassium carbonate. The oil which separated was removed, united with a portion obtained by extracting the aqueous liquor with ether, and fractionated. Thereby, *cyclobutylcarbinol*,  $\text{C}_4\text{H}_8\cdot\text{CH}_2\cdot\text{OH}$ , b. p.  $142\text{--}144^\circ/760$  mm., was obtained, together with 1:1-dimethylolcyclobutane,  $\text{C}_4\text{H}_8(\text{CH}_2\cdot\text{OH})_2$ , a viscous, pale yellow oil, b. p.  $145\text{--}147^\circ/20$  mm. H. W.

The Iodohydrin of the Glycol Derived from Cinnamyl Methyl Ether. HENRI BEAUFORT (*Bull. Soc. chim.*, 1913, [iv], 13, 349—353. Compare A., 1912, i, 621).—The iodohydrin obtained by treating cinnamyl methyl ether with iodine and mercuric oxide (*loc. cit.*) may have the formula  $\text{OH}\cdot\text{CHPh}\cdot\text{CHI}\cdot\text{CH}_2\cdot\text{OMe}$  or



The results recorded in this and the next abstract support the first formula

On treatment with powdered potassium hydroxide the iodohydrin ( $\text{D}_4^{20}$  1.500) furnishes the corresponding *oxide*,  $\text{CHPh}\cdot\text{CH}(\text{O})\cdot\text{CH}_2\cdot\text{OMe}$ .  $\text{D}_4^{20}$  1.0714, b. p.  $127\text{--}128^\circ/14$  mm., a mobile, colourless liquid with a pungent odour; it does not combine with bromine, but reacts energetically with hydriodic acid, forming an iodo-derivative which probably has the second formula quoted above.

With dimethylamine the iodohydrin yields *ω*-methoxymethylcyclohexane,

$\text{H} \cdot \text{CHPh} \cdot \text{CH}(\text{NMe}_2) \cdot \text{CH}_2 \cdot \text{OMe}$ , m. p.  $76^\circ$ ; b. p.  $152-153^\circ/12$  mm., which crystallises in colourless needles, and furnishes a *hydrochloride*, m. p.  $170^\circ$ , *hydriodide* m. p.  $102-103^\circ$ , *methiodide*, m. p.  $160^\circ$ , *picrate*, m. p.  $152-153^\circ$ , and with ethyl chloroacetate a *morpholone*, m. p.  $168^\circ$ . The *hydrochloride* of the *benzoyl* derivative, m. p.  $118^\circ$ , crystallises in spangles, has a bitter taste, and has a slow but distinct numbing action on the tongue.

T. A. II.

**Alkyl iodohydrins Derived from Cinnamyl Methyl Ether.** HENRI BEAUFOUR (*Bull. Soc. chim.*, 1913, [iv], 13, 354-358. Compare A., 1912, i, 621, and preceding abstract).—The methyl- and ethyl-iodohydrins,  $\text{OR} \cdot \text{CHPh} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OMe}$ , already described differ from the simple iodohydrin (preceding abstract) in being more stable. The methyl iodohydrin,  $\text{D}_n^\circ$  1.5070, b. p.  $160-161^\circ/15$  mm., does not react with potassium hydroxide, except in alcohol, and then furnishes at  $100^\circ$ , the *ether*,  $\text{OMe} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OMe}$ ,  $\text{D}_n^\circ$  1.0183, b. p.  $243^\circ/760$  mm.,  $128-129^\circ/13$  mm., a strongly-smelling liquid, which combines vigorously with bromine, reduces potassium permanganate solution, and when treated with steam in presence of sulphuric acid yields *phenyl vinyl ketone*,  $\text{COPh} \cdot \text{CH} \cdot \text{CH}_2$ , b. p.  $110-115^\circ/15$  mm., which readily polymerises, and yields a *dibromide*, m. p.  $55^\circ$ , crystallising in colourless needles.

The methyl iodohydrin reacts only feebly with dimethylamine at  $120^\circ$ , giving the *amine*,  $\text{OMe} \cdot \text{CHPh} \cdot \text{CH}(\text{NMe}_2) \cdot \text{CH}_2 \cdot \text{OMe}$ , b. p.  $132-133^\circ/11$  mm., whilst at higher temperatures, tarry products result.

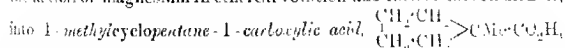
The ethyl iodohydrin ( $\text{D}_n^\circ$  1.4568) behaves like its lower homologue, and with potassium hydroxide in alcohol yields the *ethylenic ether*,  $\text{OEt} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OMe}$ ,  $\text{D}_n^\circ$  1.0428, b. p.  $137-139^\circ/15$  mm., whilst with dimethylamine it is even less reactive.

T. A. II.

**Preparation of Aromatic Amino-alcohols.** FARBENFABRIKEN FORM. FRIEDR. BAYER & Co. (D.R.P. 256750).—The previously described reduction of amino ketones in the presence of colloidal metals of the platinum group (this vol. i, 361) is found to proceed equally satisfactorily if the metal is in a state of very fine division, and the preparation of 3:4-dihydroxyphenyl- $\alpha$ -propanolamine and of 3:4-dimethoxyphenyl- $\alpha$ -propanolamine in the presence of finely-divided palladium chloride are described.

F. M. G. M.

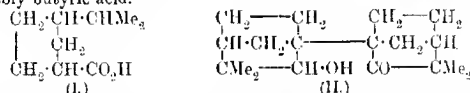
**1-Methylcyclopentane-1-carboxylic Acid.** ALEXET E. TCHERNOMIRSKY (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 184-188). —*cyclopentanone* (compare Aschan, A., 1912, i, 536) was converted into 1-methylcyclopentane-1-ol (compare Zelin-ki and Nametkin, A., 1902, i, 672), this into 1-methyl-1-chlorocyclopentane, and the latter, by the action of magnesium in ethereal solution and then of carbon dioxide, into 1-methylcyclopentane-1-carboxylic acid,



which is an unpleasant smelling liquid, b. p.  $219-220^\circ/5$  mm.,  $\text{D}_n^{20}$  1.0218,  $\text{D}_4^{20}$  1.0392. Its *silver* and *calcium* salts were analysed. The *methyl ester*,  $\text{C}_{11}\text{H}_{19}\text{O}_2$ , b. p.  $159.5^\circ/721$  mm.,  $\text{D}_n^{20}$  0.9641,  $\text{D}_4^{20}$  0.9850,  $\text{D}_n^{20}$  0.9637,  $n_D^{20}$  1.43727, and the *amide*,  $\text{C}_{11}\text{H}_{19}\text{ON}$ , m. p.  $121-125^\circ$  were prepared.

T. H. P.

**Dihydrocamphoic Acid (Camphenilic Acid)** and the Action of Sodium on Camphenilone. S. V. HINTIKKA (*Chem. Zentr.*, 1913, i, 625; from *Ann. Acad. Sci. Fennicae*, 1913, 9, 1—7).—Camphenilic acid,  $C_{18}H_{16}O_2$ , is obtained by heating camphenilone with powdered potassium hydroxide, as an oil, b. p. 140—141°/15 mm.,  $D_4^{20}$  0.9820,  $n_D^{20}$  1.45650. It forms a *chloride*, b. p. 112—114°/10 mm., a *methyl ester*, mobile oil, b. p. 203—204°/762 mm.,  $D_4^{20}$  0.9392,  $n_D^{20}$  1.44441, and an *anilide*,  $C_{25}H_{18}NO$ , in radiating needles, m. p. 89—90°. If the acid had Wallach's formula (I) it should give a hydroxy-acid on oxidation, which should further yield the lactone, dimethylnorecampholide. It undergoes extensive decomposition, however, and the products include acetic acid and probably butyric acid.



When boiled with sodium in xylene, camphenilone yields a yellow, viscous oil,  $C_{18}H_{28}O_2$  (III), b. p. 172—174°/12 mm.,  $D_4^{20}$  1.0691,  $n_D^{20}$  1.51547. J. C. W.

**Direct Hydrogenation of the Hydrocinnamic Esters: Preparation of  $\beta$ -cyclohexylpropionic Acid.** PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, 156, 751—753).—The esters of  $\beta$ -phenylpropionic acid like those of phenylacetic acid (compare this vol., i, 362) readily undergo direct hydrogenation in the presence of active nickel at 170—185°, giving the corresponding esters of  $\beta$ -cyclohexylpropionic acid in a pure state. The following have been prepared:

*Methyl  $\beta$ -cyclohexylpropionate*, b. p. 222—224° (corr.),  $D_4^{20}$  0.9705,  $D_4^{25}$  0.9603,  $n_D^{20}$  1.453.

*Ethyl  $\beta$ -cyclohexylpropionate*, b. p. 231° (corr.),  $D_4^{20}$  0.9512,  $D_4^{25}$  0.9385,  $n_D^{20}$  1.452.

*Propyl  $\beta$ -cyclohexylpropionate*, b. p. 251—252° (corr.),  $D_4^{20}$  0.9467,  $D_4^{25}$  0.9322,  $n_D^{20}$  1.455.

*isobutyl  $\beta$ -cyclohexylpropionate*, b. p. 260° (corr.),  $D_4^{20}$  0.9365,  $D_4^{25}$  0.9281,  $n_D^{20}$  1.456.

Whilst the densities decrease with increase in molecular weight the refractive indices remain practically constant. All these esters are readily saponified by warming with alcoholic potassium hydroxide, and with dilute sulphuric acid yield  $\beta$ -cyclohexylpropionic acid (compare Ipatiev, A., 1909, i, 472). W. G.

**Influence of the Nature and Position of Substituents on the Stability of the Carboxyl Group in Substituted Benzoic Acids.** FRANZ VON HEMMELMAYR (*Monatsh.*, 1913, 34, 365—385). Compare Cazeuueve, A., 1895, i, 57).—The relative stability of the carboxyl group in various substituted benzoic acids was determined by boiling the acids in solution in water or aniline and estimating the proportion decomposed in a certain time. The results, which are tabulated in detail and fully discussed, show that it is difficult to draw general conclusions as to the influence of the position of substituents on the stability of the carboxyl group. The four substituents

investigated are arranged in the following descending order as regards their effect on the stability of the carboxyl group:  $\cdot\text{OH}$ ,  $\cdot\text{NO}_2$ ,  $\cdot\text{Br}$ ,  $\cdot\text{NH}_2$ .

T. A. H.

**Preparation of Nuclear Nitroso-derivatives of Phenylglycine-*o*-carboxylic Acids, their Acids and Neutral Esters.** J. D. RIEDEL (D.R.-P. 256461. Compare A., 1887, 729, 1114; 1909, i, 794, 645).—When a cold concentrated hydrochloric acid solution of phenylglycine-*o*-carboxylic acid (5 parts) is treated with sodium nitrite, it furnishes *p*-nitrosophenylglycine-*o*-carboxylic acid hydrochloride, decomp. about  $100^\circ$ ; the free base, a green powder, condenses with *p*-nitrobenzonitrile to furnish an azomethine, red needles, m. p.  $256-258^\circ$ , and with benzonitrile to give a yellow compound.

*Dimethyl p*-nitrosophenylglycine-*o*-carboxylate has m. p.  $164-165^\circ$ , and the *diethyl* ester, m. p.  $131^\circ$ .

*p*-Nitroso-*o*-carboxymethoxyphenylglycine ethyl ester is a green, crystalline compound, m. p.  $125^\circ$ , and *p*-nitroso-*o*-carboxyphenylglycine ethyl ester has m. p.  $115-116^\circ$ .

F. M. G. M.

**Preparation of Derivatives of Arylalkyloxyacetic Acids.** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 250756. Compare McKenzie, T., 1899, 75, 755).— $\alpha$ -Ethoxy-*o*-phenylacetamide,  $\text{OEt}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$ , colourless needles, m. p.  $90^\circ$ , is obtained when ethyl ethoxyphenylacetate, b. p.  $145-147^\circ/20$  mm., is shaken with saturated ammonium hydroxide; the following derivatives have been obtained in an analogous manner.

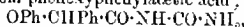
*o*-Methoxyphenylacetamide, m. p.  $110-111^\circ$ , from ethyl *o*-methoxyphenylacetate, b. p.  $148-152^\circ/22$  mm.

*p*-Tolylxyethylacetamide, m. p.  $130-131^\circ$ , from ethyl *p*-tolylxyethylacetate, b. p.  $160-165^\circ/25$  mm.

*o*-Chlorophenoxyallylacetamide, a colourless oil, b. p.  $171-174^\circ/21$  mm., from ethyl *o*-chlorophenoxyallylacetate, b. p.  $166-170^\circ/25$  mm.

Phenoxyallylacetamide, m. p.  $77-78^\circ$ , from ethyl phenoxyallylacetate, b. p.  $163-164^\circ/24$  mm.

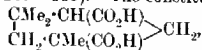
Phenoxyphenylacetamide,  $\text{OPh}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$ , colourless needles, m. p.  $154-155^\circ$ , from phenoxyphenylacetic acid; the carbamide,



colourless needles, has m. p.  $193^\circ$ .

F. M. G. M.

**Stereoisomeric *iso*Fenchocamphoric Acids.** A. E. SANDELIN (*Annalen*, 1913, 396, 285-335).—The constitution,



of *isofenchocamphoric* acid has been proved by Aschan. Theoretically, six stereoisomerides are possible, four active and two racemic. Wallach has prepared the *cis-dl*- and *l*-acids, and has shown that by mixture they produce the *cis-dl*-acid, which has been obtained by Aschan. The latter has also shown that the *cis-dl*-acid is partly changed to the *trans-dl*-acid by warming with glacial acetic and hydrochloric acids. The *trans-dl*- and *l*-acids hitherto have been unknown, but have now been prepared by the author. A large

number of derivatives of all the acids have also been prepared for comparative purposes. The two active *cis*-acids behave alike chemically, and physically, except in the sign of the rotation; the same is true of the active *trans*-acids. The fact that the *cis*-acid can be changed to the *trans*-acid, and vice versa, proves that the two are geometrical isomerides.

*trans-d*- and *l*-iso*Fenchocamphoric* acids are prepared by heating the corresponding *cis*-acids for twenty-four hours at 180–200° with a mixture of equal parts of glacial acetic acid and hydrochloric acid, D 1.20. The product, which consists of approximately equal quantities of the *trans*- and the *cis*-acids (the same product is obtained by treating the pure *trans*-acid in the same manner), is treated with acetyl chloride, and the resulting mixture of *cis*-anhydride and *trans*-acid is extracted in a Soxhlet apparatus with carbon tetrachloride, in which the *trans*-acid is insoluble. Another method of partly changing the *cis*- to the *trans*-acid is the hydrolysis of the acid chloride.

*cis-d*- and *l*-iso*Fenchocamphoric* acids crystallise in prisms, have m. p. 158–159°,  $K$  0.00492,  $[\alpha]_D^{25} + 14.58^\circ$  and  $-14.54^\circ$  respectively in alcohol, and solubility (that is, amount dissolved by 100 grams of water at 25°) 1.409 and 1.412 grams respectively; *cis-dl*-isofenchocamphoric acid crystallises in leaflets, and has m. p. 174–175°,  $K$  0.00491, and solubility 0.224. *trans-d*- and *l*-iso*Fenchocamphoric* acids crystallise in prisms, and have m. p. 149–150.5°,  $K$  0.00419 and 0.00421 respectively,  $[\alpha]_D^{25} + 4.19^\circ$  and  $-4.16^\circ$  respectively, and solubility 0.460 and 0.458 respectively; *trans-dl*-isofenchocamphoric acid crystallises in leaflets, and has m. p. 173–174°,  $K$  0.00420, and solubility 0.180.

*cis-d*- and *l*-iso*Fenchocamphoric anhydrides* crystallise in prisms, and have m. p. 98° and  $[\alpha]_D^{25} + 13.33^\circ$  and  $-13.46^\circ$  respectively in benzene; *cis-dl*-isofenchocamphoric anhydride has m. p. 95–96°. These anhydrides are easily hydrolysed by water.

All the isofenchocamphoric acids are readily esterified by the necessary alcohol and sulphuric acid, and yield, contrary to expectation, mainly the normal esters. *Methyl cis-d-isofenchocamphorate* has b. p. 253–255°, 764 mm,  $D_4^{20}$  1.0484,  $n_D^{20}$  1.45166, and  $[\alpha]_D^{25} + 19.17^\circ$ ; the *l*-ester has b. p. 253–255°/780 mm.,  $D_4^{20}$  1.0470,  $n_D^{20}$  1.45388, and  $[\alpha]_D^{25} - 19.06^\circ$ . *Methyl cis-dl-isofenchocamphorate* has b. p. 252–253°/760 mm.,  $D_4^{20}$  1.0490,  $n_D^{20}$  1.45206. *Methyl trans-d-isofenchocamphorate* has b. p. 248–249°/757 mm.,  $D_4^{20}$  1.0467,  $n_D^{20}$  1.45267,  $[\alpha]_D^{25} - 1.14^\circ$ ; the *l*-ester has the same b. p.,  $D_4^{20}$  1.0471,  $n_D^{20}$  1.45186,  $[\alpha]_D^{25} + 1.18^\circ$ . *Methyl trans-dl-isofenchocamphorate* has b. p. 247–248°/757 mm.,  $D_4^{20}$  1.0448,  $n_D^{20}$  1.45176. *Ethyl cis-d-isofenchocamphorate* has b. p. 269–271°/764 mm.,  $D_4^{20}$  1.0067,  $n_D^{20}$  1.44656,  $[\alpha]_D^{25} + 11.52^\circ$ ; the *l*-ester has b. p. 270–272°/780 mm.,  $D_4^{20}$  1.0073,  $n_D^{20}$  1.44926, and  $[\alpha]_D^{25} - 11.16^\circ$ . *Ethyl trans-d-isofenchocamphorate* has b. p. 266–267°/750 mm.,  $D_4^{20}$  1.0057,  $n_D^{20}$  1.44156,  $[\alpha]_D^{25} - 1.05^\circ$ ; the *l*-ester has the same b. p.,  $D_4^{20}$  1.0053,  $n_D^{20}$  1.44616, and  $[\alpha]_D^{25} + 0.99^\circ$ . *Ethyl trans-dl-isofenchocamphorate* has b. p. 264–265°/750 mm.,  $D_4^{20}$  1.0035,  $n_D^{20}$  1.44576.

$\alpha$ -Alkyl hydrogen isofenchocamphorates,  $\begin{matrix} \text{CMe}_2\text{CH}(\text{CO}_2\text{R}) \\ \text{CH}_2\text{CMe}(\text{CO}_2\text{H}) \end{matrix} > \text{CH}_2$ , are obtained as by-products in the esterification of the acids, and also by

the action of sodium alkoxides on the anhydrides;  $\beta$ -alkyl hydrogen esters are produced by the partial hydrolysis of the normal esters. These hydrogen esters are, almost without exception, viscous liquids which have not been obtained in a pure state. The dianilides of the *isofenchocampboric* acids are obtained from the acid chlorides and aniline in cold ether. *cis*-d- and l-*isofenchocampfordianilides* have m. p. 184—185°, and  $[\alpha]_D^{18} + 26.26^\circ$  and  $-26.53^\circ$  respectively in alcohol, and the dl-*anilide* has m. p. 142—144°. *trans*-d- and l-*isofenchocampforanilides* have m. p. 190—191° and  $[\alpha]_D - 20.30^\circ$  and  $+20.69^\circ$  respectively in alcohol, whilst the dl-*anilide* has m. p. 185—187°. It is noteworthy that the replacement of the two chlorine atoms of the acid chloride by the anilino-group yields only one of the two possible, geometrically isomeric dianilides, whereas their replacement by hydroxyl gives both *cis*- and *trans*-*isofenchocampboric* acids.

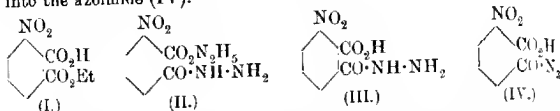
Diamides of the *cis*-acids cannot be prepared. By passing dry ammonia into a cold solution of the respective acid chlorides in ethyl acetate, *trans*-d- and l-*isofenchocampfordiamides*,  $C_{10}H_{18}O_2N_2.H_2O$ , m. p. 95—96° and 95—97° respectively,  $[\alpha]_D^{18} - 6.18^\circ$  and  $+6.37^\circ$  respectively in alcohol, and *trans*-dl-*isofenchocampfordiamide*,  $C_{10}H_{18}O_2N_2$ , m. p. 202—204°, are obtained. *cis*-d- and l-*isofenchocampforimides*, m. p. 120—121°,  $[\alpha]_D^{18} - 12.73^\circ$  and  $+12.67^\circ$  respectively in alcohol, and the dl-*imide*, m. p. 122—123°, are obtained by heating the ammonium salts of the corresponding acids at 180—200° for twenty-four hours.

$\alpha$ -*cis*-l-*isofenchocampboranic acid*,  $\begin{matrix} CMe_2-CH(CO-NH_2) \\ | \\ CH_2-CMe(CO_2H) \end{matrix} > CH_2$ , is prepared best by treating a cold ethereal solution of the *cis*-l-anhydride with dry ammonia and treating the concentrated aqueous solution of the product with hydrochloric acid. It has m. p. 220° (decomp.), decomposes when heated slowly, has  $[\alpha]_D^{20} - 11.18^\circ$  in alcohol, and yields *cis*-*isofenchocampboric anhydride* above its m. p.  $\alpha$ -*cis*-d-*isofenchocampboranic acid*, m. p. 226° (decomp.),  $[\alpha]_D^{20} + 10.99^\circ$  in alcohol, and the  $\alpha$ -*cis*-dl-*isomeride*, m. p. 208° (decomp.), are prepared by similar methods.  $\alpha$ -*trans*-d-, l-, and dl-*isofenchocampboranic acids*, m. p. 210—211°, 210—211°, and 205° respectively, are obtained as by-products in the preparation of the diamides; the active acids have  $[\alpha]_D^{18} + 7.98^\circ$  and  $-7.94^\circ$  respectively in alcohol.

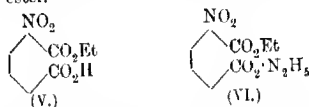
$\beta$ -*cis*-d- and l-*isofenchocampboranic acids*,  $\begin{matrix} CMe_2-CH(CO_2H) \\ | \\ CH_2-CMe(CO-NH_2) \end{matrix} > CH_2$ , m. p. 180—181°,  $[\alpha]_D^{18} + 8.91^\circ$  and  $-8.75^\circ$  respectively in alcohol, and the *cis*-dl-*isomeride*, m. p. 194—195°, are prepared by boiling the respective imides with aqueous sodium hydroxide for two hours and acidifying. The yield is quantitative, and the acids are only very slowly attacked by boiling water, crystallising therefrom in well-formed needles.  $\beta$ -*trans*-d- and l-*isofenchocampboranic acids*, m. p. 179—180°,  $[\alpha]_D^{18} + 9.71^\circ$  and  $-9.55^\circ$  respectively in alcohol, and the dl-*isomeride*, m. p. 155—156° (when crystallised from chloroform, the substance forms needles containing  $CHCl_3$ , m. p. 151—152°), are prepared by acidifying the solution obtained by boiling the respective diamides with the calculated amount of aqueous sodium hydroxide.

C. S.

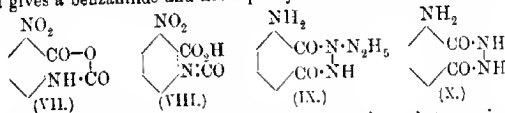
Behaviour of the 1-Ester of 3-Nitrophthalic Acid Towards Hydrazine. THEODOR CURTIUS and AUGUST SEMPER (*Ber.*, 1913, 46, 1162—1171).—Miller's monoethyl 3-nitrophthalate (I) (A., 1882, 494), the constitution of which is ascertained in the present researches, has been converted into the hydrazine salt of *o*-nitrophthalic monohydrazide (II), and this into the acid hydrazide (III), and finally into the azoimide (IV).



The latter substance loses hydrazoic acid when boiled with water or alcohol, forming *o*-nitrophthalic acid with water and the acid-ester (V) with alcohol. This isomeric acid-ester only gives a hydrazine salt with hydrazine, and, unlike the starting material, it is easily converted into the diethyl ester.

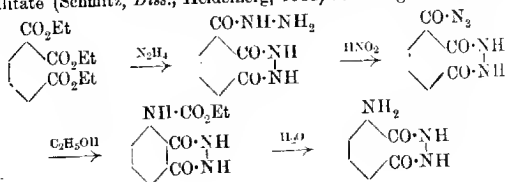


When the acid-azoimide is heated in benzene or chloroform, however, it slowly loses nitrogen and yields *o*-nitroisatoic anhydride (VII). The carbimide (VIII) might have been expected, but the substance gives, on boiling with water, not a carbanide, but 6-nitro-2-amino-benzoic acid, forms a urethane only on prolonged boiling with alcohol, and gives a benzanilide and not a phenylcarbanide with aniline.

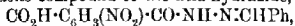


When heated with dilute sulphuric acid, the substance is also deprived of the carboxyl group and converted into *m*-nitroaniline.

If the initial acid-ester be boiled with an excess of hydrazine hydrate, the nitro-group is reduced, and water eliminated from the hydrazine salt of the monohydrazide, with the formation of the hydrazide compound (IX), which is resolved into the aminohydrazide (X) by water. This compound was also obtained from triethyl *hemi*-mellitate (Schmitz, *Diss.*, Heidelberg, 1902) according to the scheme:



For the preparation of the *hydrazine* salt of *o*-nitrophthalic acid *monohydrazide* (II), Miller's ester, m. p.  $110^{\circ}$ , is triturated with hydrazine hydrate. It forms colourless needles, m. p.  $157^{\circ}$ , which yield the *benzylidene* compound of the acid-hydrazide,



in small, colourless needles, m. p.  $177^{\circ}$ , and, with hydrochloric acid, the *acid hydrazide* (III), in flat needles, m. p. above  $280^{\circ}$ , from which the *azoimide* (IV) is obtained in colourless, shimmering scales by the addition of sodium nitrite to the suspension in concentrated hydrochloric acid. After prolonged boiling with absolute alcohol the azoimide is converted into the *acid-ester* (V), which forms yellow needles, m. p.  $157^{\circ}$ , but when heated in dry chloroform the product is *o*-nitroisatoic anhydride (VII), which crystallises in pale yellow, flat needles, m. p.  $215^{\circ}$ , and is isomeric with Kolbe's nitroisatoic anhydride (A., 1885, i, 666), which gave 5-nitro-2-aminobenzoic acid on boiling with water. It gradually dissolves in boiling absolute alcohol, forming the *urethane*,  $\text{C}_{10}\text{H}_9\text{O}_6\text{N}_3$ , in faintly yellow, flat needles, m. p.  $187^{\circ}$ , which yield *m*-nitroaniline with dilute acids. It also forms the *anilide*,  $\text{C}_{13}\text{H}_{11}\text{O}_5\text{N}_3$ , in slender, yellow needles, m. p.  $137^{\circ}$ .

The *hydrazine* salt of the cyclic *hydrazide* of *o*-aminophthalic acid (IX) results when the starting material is heated with an excess of hydrazine hydrate. The free *hydrazide* (X) is a yellow solid, which behaves as a monobasic acid, forming *barium*, *potassium*, and *sodium* salts. It is also soluble in dilute acids, and gives a blue fluorescence in hot glacial acetic acid (compare Schmitz, *loc. cit.*).

J. C. W.

**Preparation of  $\alpha\beta$ -Diketonic Esters.** ANDRÉ WAHL and M. DOLL (*Bull. Soc. chim.*, 1913, [iv], 13, 332—348. Compare A., 1904, i, 556; 1907, i, 217; 1911, i, 108; 1912, i, 536, 625).—This paper discusses in detail the mechanism of the reaction between "nitrous fumes" and acylacetic esters, by means of which the methylene group of the latter is converted into a carbonyl group, with the formation of  $\alpha\beta$ -diketonic esters. Examples of this reaction have been recorded already (*loc. cit.*). The reaction occurs in two stages: (1) the formation of an oximino-derivative of the acylacetate (A., 1904, i, 556; 1905, i, 409), and (2) the conversion of this oximino-derivative into the corresponding  $\alpha\beta$ -diketonic ester by the action of "nitrous fumes." The latter were obtained by treating "chamber crystals" with sodium nitrite, and as applied consisted chiefly of  $\text{N}_2\text{O}_3$  and  $\text{NO}_2$  (89.2%) with some  $\text{NO}$  (10%). The gas resulting from the second phase of the reaction was chiefly  $\text{N}_2$  (54%),  $\text{N}_2\text{O}_3 + \text{NO}_2$  (29%),  $\text{N}_2\text{O}$  (10%), and  $\text{NO}$  (7%), so that this phase is not unilateral. The following new compounds were prepared.

*Methyl benzoylglyoxylate*,  $\text{D}_0^{\circ}$  1.233, b. p.  $146-149/12$  mm., is a mobile, orange-yellow liquid, which reduces Fehling's solution and ammoniacal silver nitrate, and yields a *hydrate*,  $\text{COPh}\cdot\text{CO}\cdot\text{CO}_2\text{Me}\cdot\text{H}_2\text{O}$ , m. p.  $65^{\circ}$ , crystallising in stellate groups of pearly needles. *Propyl benzoylglyoxylate*, b. p.  $155-158/12$  mm.,  $\text{D}_0^{\circ}$  1.159, combines with alcohol or water, but the products are not crystalline. *isoButyl*



*benzoylglucosylate*, D<sup>o</sup> 1.124, b. p. 161—164°/12 mm., yields a crystalline *monohydrate*, m. p. 62—63°.

*Ethyl valerolglucosylate*, b. p. 100—125°/15 mm., was not obtained pure. T. A. H.

**Synthesis of Orsellinic Acid and Everninic Acid.** KURF HORSCH (Ber., 1913, 46, 886—892).—Attempts to synthesise orsellinic acid from orcinol by a process analogous to the salicylic acid synthesis yielded only the isomeric *p*-orsellinic acid. The synthesis could, however, be successfully effected by the oxidation of orcylaldehyde.

Orcylaldehyde, obtained from orcinol by the method of Gattermann (A., 1908, i, 28), was found to undergo oxidation more smoothly after converting the hydroxyl groups into methylcarbonato-groups (compare Fischer and Freudenberg, A., 1910, i, 265) by the action of methyl chlorocarbonate and sodium hydroxide. *Dimethylcarbonato-orcylaldehyde*,  $\text{CHO} \cdot \text{C}_6\text{H}_2\text{Me}(\text{O} \cdot \text{CO}_2\text{Me})_2$ , crystallises in needles, m. p. 84—85°, which turn yellow on exposure to light; *methylcarbonato-orcylaldehyde*,  $\text{CHO} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OH}) \cdot \text{O} \cdot \text{CO}_2\text{Me}$ , obtained by the action of less methyl chlorocarbonate forms prisms, m. p. 79°. *Diethylcarbonato-orcylaldehyde*, needles, m. p. 60°, obtained analogously to the corresponding dimethylcarbonato-compound, behaves similarly to the latter towards oxidation; when treated in acetone solution at 40° with potassium permanganate, they are oxidised to dimethylcarbonato-orsellinic acid (compare Fischer and Hoesch, A., 1912, i, 859) and *diethylcarbonato-orsellinic acid*, prisms, m. p. 113° (decomp.) respectively. These acids are hydrolysed by *N*-sodium hydroxide solution at room temperature, giving satisfactory yields of orsellinic acid,  $\text{C}_6\text{H}_2\text{Me}(\text{OH})_2 \cdot \text{CO}_2\text{H}$ .

If orcylaldehyde is cautiously methylated by methyl sulphate and 2*N*-sodium hydroxide in acetone solution, *everninaldehyde* (2-hydroxy-4-methoxy-6-methylbenzaldehyde) is obtained as needles, m. p. 65°. When heated with anhydrous sodium acetate and acetic anhydride in a sealed tube for five hours at 170—180°, everninaldehyde is converted into 7-methoxy-5-methyl-1:2-benzopyrone,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me} \begin{smallmatrix} \text{CH}=\text{CH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{smallmatrix}$ , long needles, m. p. 146°, which dissolve in concentrated sulphuric acid, giving a blue fluorescence; the success of this synthesis confirms the structure already assumed for everninaldehyde (Fischer and Hoesch, loc. cit.). When an acetone solution of everninaldehyde is carefully treated with methyl chlorocarbonate and sodium hydroxide, *methylcarbonatoeverninaldehyde*,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}(\text{O} \cdot \text{CO}_2\text{Me}) \cdot \text{CHO}$ , needles, m. p. 77°, which redden in the light and are phototropic, is obtained. This is oxidisable by potassium permanganate with care to methylcarbonato-everninic acid, silky needles, which decompose near 100°, and can be hydrolysed by *N*-sodium hydroxide at the ordinary temperature to everninic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OH}) \cdot \text{CO}_2\text{H}$ . D. F. T.

**Hydrogenation of Santonin.** HEINRICH WIENHAUS and WOLFGANG FELIX VON OETTINGEN (Annalen, 1913, 397, 219—246).—By reduction by the Paal-Anleberger method, santonin absorbs four atomic proportions of hydrogen, and yields two stereoisomeric tetra-

hydrosantonins. Hence the formulæ of Cannizzaro and Andreocci and of Angeli and Marino, which contain only one ethylenic linking, are disproved. The formulæ of Cannizzaro and Gucci and of Francesconi and Cusmano (A., 1908, i. 272) are permissible, and of the two, the former,  $\text{CH}_2\cdot\text{CMe}\cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}\text{---}\text{O}$   $\text{CO}\cdot\text{CMe}=\text{C}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}$   $\text{>CO}$ , is preferable.

When the hydrogenation of santonin is discontinued after 1 mol. of hydrogen has been absorbed, it is found, in accord with Paal's experience with substances containing a conjugated system (A., 1912, i. 703), that the addition does not occur in the sense of Thiele's theory; in other words, one half of the santonin is completely reduced, the other half is unattacked.

Santonin is so readily reduced that 50 grams in methyl alcohol, in the presence of 1 gram of palladous chloride, absorbed 10 litres (at 15° and 745 mm.) of hydrogen in ten minutes; the reduction proceeds even with flocculent (non-colloidal) palladium. The products are  $\alpha$ - and  $\beta$ -tetrahydrosantonins, the separation of which is effected by taking advantage of the very slight tendency of  $\beta$ -tetrahydrosantoninic acid (see below) to lactone formation.

$\alpha$ -Tetrahydrosantonin,  $\text{C}_{15}\text{H}_{22}\text{O}_3$ , m. p. 158°, colourless, rectangular leaflets, does not become yellow in light, is unchanged by the action of zinc-dust and warm acetic acid, and forms an *oxime*, m. p. 235–237°, and *semicarbazone*, m. p. 256–258° (decomp.).  $\beta$ -Tetrahydrosantonin,  $\text{C}_{15}\text{H}_{22}\text{O}_3$ , m. p. 105°, stout plates, forms an *oxime*, m. p. 182°, and *semicarbazone*, m. p. 248–250° (decomp.).

During the reduction of anhydrous santoninoxime by the Paal-Amberger method, the oximino-group is attacked, since ammonia and  $\alpha$ -tetrahydrosantonin have been isolated from the products. The reduction of aqueous sodium santonate in a similar manner yields  $\alpha$ -tetrahydrosantoninic acid,  $\text{C}_{15}\text{H}_{20}\text{O}_4\text{H}_2\text{O}$ , m. p. 115° (decomp.) (anhydrous, 135–145°), rhombohedral crystals (sodium salt, colourless needles or leaflets), and  $\beta$ -tetrahydrosantoninic acid,  $\text{C}_{15}\text{H}_{20}\text{O}_4$ , m. p. 200° (decomp.), or 192° slowly heated, colourless plates, which form an *oxime*,  $\text{C}_{15}\text{H}_{20}\text{O}_4\text{N}$ , m. p. 218–220°.

By warming with aqueous sodium hydroxide or carbonate and then acidifying,  $\alpha$ -tetrahydrosantonin is converted into  $\alpha$ -tetrahydrosantoninic acid, which is readily changed back to the lactone by heating, or by keeping its ethereal solution. In a similar manner,  $\beta$ -tetrahydrosantonin is converted into  $\beta$ -tetrahydrosantoninic acid. This acid is more stable than the  $\alpha$ -isomeride, but is re-converted into  $\beta$ -tetrahydrosantonin by heating at 200° under reduced pressure.

Attempts to convert  $\alpha$ -tetrahydrosantonin or the acid into the corresponding  $\beta$ -compounds, and vice versa, have been unsuccessful.

Whilst santonin itself has  $[\alpha]_{\text{D}}^{20} \sim 171\cdot70^\circ$  in methyl alcohol,  $\alpha$ -tetrahydrosantonin has a mean value  $+17\cdot1^\circ$  ( $[\alpha]_0$  of the oxime in chloroform increases from  $-38\cdot05^\circ$  to  $-53\cdot07^\circ$  with increase of the concentration from 1·63% to 3·34%);  $\beta$ -tetrahydrosantonin has  $[\alpha]_0 +41\cdot08^\circ$  when prepared directly from santonin and  $9\cdot27^\circ$  when obtained from the  $\beta$ -acid;  $\alpha$ -tetrahydrosantoninic acid has  $[\alpha]_0 +20\cdot00^\circ$ , and the  $\beta$ -acid has  $[\alpha]_0 +2\cdot18^\circ$  (both prepared from the sodium salts).

C. S.

**Santonin. XI. Tetrahydrosantonin.** EDGAR WEDEKIND and E. BENIERS (*Annalen*, 1913, 397, 246—254. Compare A., 1908, i, 183).—Many of the authors' results are identical with those obtained by Wienhaus and von Oettingen (preceding abstract). However, by the reduction of santonin in acetone by hydrogen ( $1\frac{1}{2}$  atmospheres) in the presence of palladous chloride and gum arabic, they have been unable to isolate  $\beta$ -tetrahydrosantonin. The m. p. of  $\alpha$ -tetrahydro-santoninoxime is given as 219—220°, and that of the *phenylhydrazones* as 205° (decomp.).  $\alpha$ -Tetrahydrosantonin and nitric acid, D 1.4, yield  $\alpha$ -dinitrotetrahydrosantonin,  $C_{15}H_{20}O_7N_2$ , decomp. 187°, large, colourless plates,  $[\alpha]_D + 105.05^\circ$  in alcohol and 90.22° in chloroform.

By bromination in chloroform at 35—40°,  $\alpha$ -tetrahydrosantonin yields  $\alpha$ -bromotetrahydrosantonin,  $C_{15}H_{21}O_3Br$ , decomp. 147°, colourless, prismatic needles,  $[\alpha]_D + 9.09^\circ$  in chloroform. C. S.

**Preparation of 1-Aminoanthraquinone-2-carboxylic Acids and their Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 256344. Compare A., 1912, i, 979).—*Ethyl 1-op-dichloroanilino-anthraquinone-2-carboxylate*, coppery-red needles, is obtained when *ethyl 1-chloroanthraquinone-2-carboxylate* (yellow leaflets, m. p. 142°) is boiled for five to six hours with *op*-dichloroaniline in nitrobenzene solution in the presence of cuprous chloride and sodium acetate; the free acid obtained by its hydrolysis (alcoholic potassium hydroxide) is a scarlet-red powder. *Methyl 1-chloroanthraquinone-2-carboxylate*, m. p. 164°, can also be employed in this reaction. *Ethyl 1:1'-anthraquinonylaminoanthraquinone-2-carboxylate* forms scarlet-red needles and the free acid a violet powder, whilst the isomeric compounds from *ethyl 1-chloroanthraquinone-2-carboxylate* with 2-aminoanthraquinone consist of orange-yellow leaflets and a red powder respectively. The compound from 1-amino-4-hydroxyanthraquinone and *ethyl 1-chloroanthraquinone-2-carboxylate* forms violet-blue needles.

*Ethyl 1-nitroanthraquinone-2-carboxylate*, yellow leaflets, m. p. 232—233°, when condensed with *op*-dichloroaniline gives rise to a compound, dark red needles; the free acid is a red powder.

F. M. G. M.

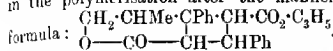
**Esters of Polycinnamic Acid.** CARL LIEBERMANN and M. KARDOS (*Ber.*, 1913, 46, 1055—1066).—In continuation of previous work (A., 1911, i, 370) on the polymerisation of esters of cinnamic acid, the authors have investigated the two allyl polycinnamates described by Seeligmann (*Diss.*, Karlsruhe, 1906). These two esters, which are termed allyl polycinnamate *A* and *B*, are formed by heating allyl cinnamate in sealed tubes at 210°.

The ester *A* is obtained by heating for six hours, and isolated from the resulting liquid by dissolving in benzene and precipitating with a mixture of alcohol and ether. It separates in heavy, white flocks, sintering at 190—200°, but possesses no definite m. p.

The ester *B* is best prepared by heating allyl cinnamate for fifteen hours and extracting the product with benzene, when it is obtained as a white powder, which becomes brown and decomposes at about

300°; it differs from the ester *A* in being insoluble in benzene and chloroform.

The two polymerides are hydrolysed by boiling with 25% alcoholic potassium hydroxide, but the amount of allyl alcohol produced is only 10–12% of that to be expected on the assumption that the polymerides are allyl esters of polycinnamic acid  $(C_9H_8O_2)_x$ . The conclusion is therefore drawn that the double linking of the allyl groups takes part in the polymerisation after the manner indicated in the following formula:



This view is also confirmed by the behaviour of the ester *A* towards bromine. It combines with bromine very slowly, and after twenty-four hours yields a *bromo*-compound,  $(C_{15}H_{12}O_2Br)_x$ , the amount of bromine uniting with the ester being only half that which would have been combined had the allyl groups remained intact.

Both polymerides are hydrolysed by alcoholic potassium hydroxide to the corresponding *acids*, which form white, amorphous powders, sintering at 180–190° (decomp. 210–220°), and closely resemble one another.

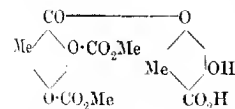
The above esters differ from that obtained by the polymerisation of allyl cinnamate by exposure to light, in solubility, and in being hydrolysed by alkalis.

Allyl cinnamate combines almost instantly with bromine (1 mol.) in chloroform solution, yielding *αβ*-dibromopropyl cinnamate as a viscous oil. Combination with a second molecule takes place more slowly, resulting in the formation of *αβ*-dibromopropyl *αβ*-dibromopropionate, which crystallises in white needles, m. p. 69–71°.

On exposure to light for nine months, allyl cinnamate yields a *polymeride*, which is precipitated by methyl alcohol in white flocks, m. p. above 300°, and is not hydrolysed by alcoholic potassium hydroxide.

The *polymerides* of benzyl cinnamate (decomp. 270°) and octyl cinnamate have been prepared in a similar manner. F. B.

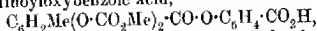
**Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations.** VIII. Derivatives of Orsellinic and *α*-Resorcylic [3:5-Dihydroxybenzoic] Acids. EMIL FISCHER and HERMANN O. L. FISCHER (*Ber.*, 1913, **46**, 1138–1148).—The difficulties attendant on the conversion of dimethylcarbonato-orsellinic acid (3:5-dimethylcarbonato-*o*-toluic acid) into its chloride have been overcome (compare A., 1912, i, 860). By



coupling the latter with orsellinic acid, the authors have been able to prepare dimethylcarbonato-orsellinoylorsellinic acid (annexed formula), which, when hydrolysed, gives a *thorsellinic acid* identical with the natural lecanoric acid. A series of compounds has also been prepared from *α*-resorcylic acid.

*Dimethylcarbonato-orsellinyl chloride*,  $C_8H_2Me(O \cdot CO_2Me)_2 \cdot COCl$ ,

m. p. 53—54°, is obtained by the action of phosphorus pentachloride on dimethylcarbonato-orsellinic acid suspended in chloroform. In suitable circumstances it reacts readily with ethyl alcohol, the corresponding *ethyl* ester being probably formed. In alkaline acetone solution it condenses with *p*-hydroxybenzoic acid, forming 4-dimethylcarbonato-orsellinoyloxybenzoic acid,



m. p. 203—205° (corr. decomp.), after previous softening at about 190°, which in aqueous alcoholic solution does not give a characteristic coloration with ferric chloride. The alkaline salts are sparingly soluble in water. When heated with ammonia, the dipeptide, 4-*orsellinoyloxybenzoic acid*, is obtained. Difficulty was experienced in obtaining the latter in the crystalline form until a nucleus of the crystalline acid was isolated by decomposition of the *pyridine* salt. The air-dried acid contains 1H<sub>2</sub>O. It has m. p. about 209° (corr. decomp.) after previous softening at about 180°, the value found depending greatly on the mode of heating.

*Dimethylcarbonato-orsellinoylorsellinic acid*, needles, m. p. 185—187° (corr. decomp.), is obtained by the gradual addition of a solution of dimethylcarbonato-orsellinoyl chloride in acetone to a well-cooled solution of orsellinic acid in acetone and *N*-sodium hydroxide. In aqueous alcoholic solution it gives an intense reddish-violet coloration with ferric chloride. By repeated treatment with methyl chloroformate and alkali in aqueous acetone solution, it yields a crystalline *product*, which gives no coloration with ferric chloride. This can be separated by means of potassium carbonate into a soluble portion, probably *trimethylcarbonatolecanoric acid*, and an insoluble portion which is being investigated. Aqueous sodium hydroxide slowly converts dimethylcarbonato-orsellinoylorsellinic acid into lecanoric acid, colorless needles, having no definite m. p. When quickly heated it softens at about 170°, and is completely melted at 175° with brisk evolution of gas. The air-dried acid contains 1H<sub>2</sub>O. Identity of this product with natural lecanoric acid was established by comparison of m. p., colorations with ferric chloride and bleaching powder, solubility, and crystal form of the two substances, and, further, by the transformation of each into the *trimethyl ether* of *methyl lecanorate*, C<sub>20</sub>H<sub>20</sub>O<sub>8</sub>. The product from the synthetic acid had m. p. 147—148° (corr.), whilst that from the natural acid had m. p. 146—147° (corr.) after softening at 140°. A mixture of the two had m. p. 145—146.5°.

3:5-*Dimethylcarbonatobenzoic acid*, prepared by the action of methyl chlorocarbonate on a solution of 3:5-dihydroxybenzoic acid in *N*-sodium hydroxide, has m. p. 161—164° (corr.) after slight previous softening. Phosphorus pentachloride converts it into the corresponding *chloride*, colorless needles, m. p. 109—110° (corr.), which, when coupled with *p*-hydroxybenzoic acid in the usual manner, yields 4-(3:5-dimethylcarbonatobenzyloxy)benzoic acid, C<sub>6</sub>H<sub>3</sub>(O·CO<sub>2</sub>Me)<sub>2</sub>·CO·O·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, needles, m. p. 161—163° (corr.).

When treated with aluminium chloride and benzene during an hour at 70—75°, and then during forty-five minutes at 75—80°, 3:5-dimethylcarbonatobenzoyl chloride yields 3:5-dihydroxybenzophenone, which separates from water with 1H<sub>2</sub>O. The dry substance has m. p.

160–162° (corr.). If the temperature in the above process is maintained at 40–45° during five hours, no hydrogen chloride is evolved, and a pale yellow oil is subsequently obtained, which crystallizes when brought into contact with light petroleum. The product, which has not yet been obtained in the pure state, contains the methyl-carbonato-groups, and is transformed by alkali into 3:5-dihydroxybenzophenone.

H. W.

Tannin and the Synthesis of Similar Substances. III. Compounds of High Molecular Weight. EMIL FISCHER and KURT FREUDENBERG (*Ber.*, 1913, 46, 1116–1133).—The authors have continued their previous work (*A.*, 1912, i, 471, 887), and describe a convenient method of preparing *m*-digallic acid in larger quantities. The properties of this acid resemble those of the digallic acid previously described as the para-compound (*A.*, 1908, i, 893) so closely that the two substances are in all probability identical. It differs considerably, however, from the *m*-digallic acid described by Nierenstein (*A.*, 1910, i, 265).

A series of compounds of high molecular weight has been obtained by the use of tribenzoylgallic acid; for example, hexa-(tribenzoylgalloyl)-mannitol. In the analysis of this and similar compounds, a difficulty is experienced in that the differences in the percentages of carbon and hydrogen are not sufficiently great to allow conclusions to be drawn with regard to the number of acyl groups present. This has been overcome by the introduction of halogen atoms into the molecule, and a series of substances has been prepared from 2:4:6-tribromophenol-*d*-glucoside and *p*-iodophenylmaltosazone, of which the most interesting is hepta-(tribenzoylgalloyl)-*p*-iodophenylmaltosazone,



mol. wt. 4021. The molecular weight of this and similar substances has been determined in bromoform solution, the observed values being found to agree with those theoretically required without greater divergence than is frequently encountered with much more simply constituted, crystalline substances.

*Carbonylgallic acid* (4:5-carbonato-3-hydroxybenzoic acid),  $\text{OC} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{C}_6\text{H}_2(\text{OH})\cdot\text{CO}_2\text{H}$ , is obtained by the addition of a solution of carbonyl chloride in toluene to a well-cooled mixture of gallic acid, acetone, and 2*N*-sodium hydroxide (3 mols.), and subsequent acidification of the product with hydrochloric acid. A full description of the apparatus employed is given. The acid has m. p. about 255° (corr. decomp.). It is sparingly soluble in cold water, and decomposed by hot water with regeneration of gallic acid. Hot methyl alcohol converts it into 3-methylcarbonatogallic acid. In alcoholic solution it gives a faint coloration with ferric chloride, which increases in intensity on keeping. It is transformed by diazomethane into methyl 4:5-carbonato-3-methoxybenzoate,  $\text{OC} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{C}_6\text{H}_2(\text{OMe})\cdot\text{CO}_2\text{Me}$ , long needles, m. p. 134° (corr.), which, when boiled with water, probably yields methyl 4:5-dihydroxy-3-methoxybenzoate. The latter is converted by the successive action of sodium hydroxide and hydro-

chloric acid into 4:5-dihydroxy-3-methoxybenzoic acid, which is apparently identical with the acid obtained by Vogl (A., 1899, i, 698). The latter gives m. p. 199—200° (uncorr.), whereas the authors find about 220° (corr. decomp.), but point out that the observed m. p. depends greatly on the mode of heating.

*m*-Digallic acid is prepared by the alternate addition of *N*-potassium hydroxide and of a solution of trimethylcarbonatogalloyl chloride in acetone to a cooled solution of carbonylgallic acid in acetone and *N*-potassium hydroxide. The product is treated with *N*-sodium hydroxide and subsequently with hydrochloric acid, when *m*-digallic acid, needles, m. p. about 280° (corr. decomp.) after softening at 260° (corr.), is obtained, the yield being 45% of the theoretical. The acid dissolves in water at 25° in the proportion 1:860, and gives a deep bluish-black coloration with ferric chloride. With aqueous potassium cyanide solution, it yields, after ten seconds, a pink coloration which disappears after a time, but returns on shaking the solution. When boiled during six hours with 1% hydrogen peroxide solution, it yields a dark brown coloration, but no precipitate. With 10% aqueous hydrogen peroxide under similar conditions, a clear solution is formed. In these particulars, the acid differs markedly from Nierenstein's *m*-digallic acid (*loc. cit.*). With diazomethane, it yields methyl 5(3':4':5')-trimethoxybenzoyloxy-3:4-dimethoxybenzoate, which is identical with the product obtained previously (A., 1912, i, 888). Acetic anhydride converts it into *penta-acetyl-m-digallic* acid, needles, m. p. 193—194° (corr.), after softening at about 184° (Nierenstein's *m*-digallic acid gave a *penta-acetyl* derivative, m. p. 211—214°). An attempt to prepare the corresponding pentabenzoyl derivative was unsuccessful.

3:4:5-Trimethoxybenzoic anhydride, microscopic needles, m. p. 160—161° (corr.), is obtained by the action of 3:4:5-trimethoxybenzoyl chloride on 3:4:5-trimethoxybenzoic acid in chloroform solution in the presence of quinoline. Similarly, the mixed anhydride of 3:4:5-trimethoxybenzoic acid and pentamethyl-digallic acid, needles, m. p. 165—166° (corr.), is obtained from 3:4:5-trimethoxybenzoyl chloride and pentamethyl-*m*-digallic acid, and is identical with a product previously obtained during the synthesis of pentamethyl-*m*-digallic acid (A., 1912, i, 888).

*Pentamethyl-p-digallic* acid is formed in 75% yield from 3:4:5-trimethoxybenzoyl chloride and syringic acid according to the method employed in preparing the *m*-isomeric. It forms leaflets, m. p. 221—222° (corr.). The methyl ester, prepared by the action of diazomethane on the acid, has m. p. 172—173° (corr.), whereas Mauthner (A., 1911, i, 725) found m. p. 169—170°.

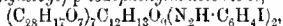
*Tribenzoylgalloyl chloride*,  $C_6H_5(OBz)_3 \cdot COCl$ , needles, m. p. 124—125° (corr.), is obtained by the action of phosphorus pentachloride on tribenzoylgallic acid in the presence of chloroform at the ordinary temperature. The corresponding ethyl ester has m. p. 126—128° (corr.), whilst the anhydride,  $C_{26}H_{34}O_{15}$ , needles, has m. p. 195—196° (corr.) and is more stable towards alcohol than simple substances of this class.

*Tetra-(tribenzoylgalloyl)-tribromophenol-d-glucoside*,  
 $(C_{28}H_{17}O_7)_4 \cdot C_6H_2O_6 \cdot C_6H_2Br_3$ ,

is prepared by the addition of trihromophenol-*d*-glucoside to a solution of tribenzoylgalloyl chloride and quinolin in chloroform. It is a white, amorphous powder, which softens at about 130°, and melts to a clear syrup at about 155°. In tetrachloroethane solution, it has  $[\alpha]_D^{25} = -31.01^\circ$ . Hexa-(tribenzoylgalloyl)-mannitol, obtained in a similar manner, has  $[\alpha]_D^{25} + 19.63^\circ$  in tetrachloroethane solution. It softens at about 125°, and is completely molten at about 150°.

Tetribenzoylphenylglucosazone,  $C_{66}H_{60}O_4Bz_4(N_2HPh)_2$ , softens at about 100°, is completely molten at about 130°, and begins to decompose at about 140°. When dissolved in acetylene tetrachloride, it has  $[\alpha]_D^{25} = 12.16^\circ$  for the Auer light.

*p*-Iodophenylmaltosazone,  $C_{12}H_{20}O_5(N_2H \cdot C_6H_4I)_2$ , prepared by the action of *p*-iodophenylhydrazine on maltosone in aqueous-alcoholic solution, crystallises in yellow needles, m. p. 203° (corr.), after slight previous softening, the m. p., however, varying according to the mode of heating. The solution in pyridine exhibits mutarotation, constant values being probably obtained after three days. For one specimen,  $[\alpha]_D^{25}$  was found to be  $+83.44^\circ$  after eight minutes,  $+66.51^\circ$  after thirty-two hours,  $+66.11^\circ$  after forty-eight hours. When treated with tribenzoylgalloyl chloride at the ordinary temperature in the presence of quinoline and chloroform, *p*-iodophenylmaltosazone yields hepta-(tribenzoylgalloyl)-*p*-iodophenylmaltosazone,



amorphous, pale yellow powder, which softens at about 145°, and is melted to a red liquid at 160°. In tetrachloroethane solution it has  $[\alpha]_D^{25} = 8.75^\circ$ .

The molecular weight of the above substances of high molecular weight was determined cryoscopically in bromoform solution, care being taken to obtain them free from any trace of adhering solvent. From experiments on the molecular weight of naphthalene dissolved in bromoform, the value 143 was adopted as constant for the solvent. The following mean results were obtained, the theoretical values being enclosed in brackets: tribenzoylgallic anhydride, 954 (946); tetra-(tribenzoylgalloyl)-tribromophenol-*d*-glucoside, 2036 (2348); hexa-(tribenzoylgalloyl)-mannitol, 2781 (2967); hepta-(tribenzoylgalloyl)-*p*-iodophenylmaltosazone, 3503 (4021).

H. W.

Salicylaldehydphenylhydrazone. GEORG LOCKEMANN and FRANZ LUCIUS (*Ber.*, 1913, 46, 1012—1021. Compare this vol., i, 296).—Salicylaldehyde phenylhydrazono (compare Biltz, *A.*, 1894, 584) can appear in isomeric forms, which, however, do not differ in melting point, but in crystalline form, colour, and solubility. Their formation depends on the conditions of crystallisation and the illumination. The isomerism is therefore physical and not chemical, as supposed by Biltz.

The  $\alpha$ -hydrazone is formed in rectangular prisms on slow crystallisation from dilute alcohol or benzene; these are pale or dark green when light is excluded, greyish or brownish-yellow in its presence. The green form occurs in presence of acetic acid; with ammonia the yellow modification is formed.

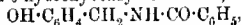
The  $\beta$ -hydrazone is deposited on quick crystallisation in colourless



needles, which become greenish-yellow on exposure to light. The  $\gamma$ -modification separates from light petroleum in bunches of green needles, which become yellow or orange on exposure. In all three modifications the coloration brought about by light slowly reverses in the dark. All three soften between  $135^{\circ}$  and  $140^{\circ}$ , m. p.  $142-143^{\circ}$ .

When benzoylated in pyridine solution, according to the proportion of benzoyl chloride, the *O*-monobenzoyl or the *O,N*-dibenzoyl derivatives are obtained. When sodium hydroxide is present, the dibenzoyl derivative is the main product, more or less hydrazone remaining unattacked.

On reduction of the dibenzoyl derivative with zinc dust and acetic acid, benzanilide and *o*-hydroxybenzylbenzamide,



are formed.

*o*-Benzoylhydroxybenzylbenzamide, prepared by benzoylating by the Schotten-Baumann process, forms colourless needles, m. p.  $141-142^{\circ}$ .

When hydrolysed either with cold alcoholic potassium hydroxide or warm alcoholic ammonia, *N*-benzoyl-*o*-hydroxybenzaldehydephenyl hydrazone is obtained; it gives a dark bluish-green ferric chloride coloration.

E. F. A.

**Condensation Product of Piperonaldehyde with Ethyl Urethane.** I. G. BIANCHI (*Gazzetta*, 1913, 43, i, 237-243).—

When these substances are heated for half an hour on the water-bath with a little hydrochloric acid, piperonylidenebisurethane,  $\text{C}_{12}\text{H}_{18}\text{O}_5\text{N}_2$ , m. p.  $177-178^{\circ}$ , is obtained; it crystallises in colourless needles.

R. V. S.

**Preparation of Cyclic Ketones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 256622).—When adipic acid, its homologues, or substitution products are heated they furnish satisfactory yields of the corresponding cyclic ketones; this reaction is conveniently carried out under reduced pressure, in the presence of an inert gas, and of a catalytic reagent, such as oxides, carbonates or other salts of the alkali metals, alkaline earths, or magnesium; of salts of the heavy metals, such as iron, nickel, cobalt, manganese, or uranium; or of phosphoric, boric, or other acids.



*cyclo*Pentanone, b. p.  $49-50^{\circ}/31$  mm., is obtained in quantitative yield from adipic acid at  $290-295^{\circ}$  in the presence of barium hydroxide; with uranium nitrate the yield is 85%, and with ferrous sulphate 90%.

2-Methylcyclopentanone, b. p.  $38^{\circ}/11$  mm. and  $57-59^{\circ}/29$  mm., is similarly obtained at  $300-305^{\circ}$  from  $\beta$ -methyladipic acid, whilst suberic acid furnishes suberone (b. p.  $179^{\circ}$ ) at  $320-325^{\circ}$  in the presence of iron.

F. M. G. M.

**Terpenes and Etheral Oils.** CXV. OTTO WALLACH (*Annalen*, 1913, 397, 181-219).—A systematic examination has hitherto not been made of the problem how the position of the oxygen atom in a cyclic ketone influences the b. p. Recent examples in the literature

lead the author to the generalisation that in saturated, isomeric, cyclic ketones containing the same substituents the b. p. is lowest when the heaviest substituent is nearest to the oxygen atom and highest when this substituent is situated as far as possible from the oxygen atom. Since dihydroisocamphor has b. p.  $211^{\circ}$  and carvomenthone has b. p.  $220-221^{\circ}$ , the generalisation furnishes corroborative evidence that dihydroisocamphor is not 1-methyl-5-isopropylcyclohexan-2-one (compare A., 1912, i, 878).

Much more complicated and difficult is the problem of the relations between the constitutions and the b. p.'s of unsaturated cyclic ketones, since in such substances the position of the ethylenic linking must also be taken into account. By reference to the b. p.'s and the constitutions of many unsaturated cyclic ketones, the author shows that (i) ketones in which the ethylenic group and the carbonyl group form a conjugated system have a higher b. p. than isomeric ketones in which such a system does not obtain, and, moreover, that the b. p. is higher when the ethylenic linking in the conjugated system is part of the carbocyclic nucleus than when it is attached semicyclically or is present in a side-chain; for example,  $\Delta^1$ -menthen-3-one, b. p.  $235^{\circ}$ , pulegone, b. p.  $221-222^{\circ}$ , and also carvenone, b. p.  $232-233^{\circ}$ , and dihydrocarvone, b. p.  $221-223^{\circ}$ ; (ii) the replacement of the hydrogen atom in the system  $\text{C}:\text{CH}\cdot\text{CO}\cdot$  by an alkyl group R is accompanied by a fall in the b. p. which is the more pronounced the greater is the molecular weight of R; for example, 1-methyl-5-isopropyl- $\Delta^1$ -cyclohexen-3-one, b. p.  $244^{\circ}$ ,  $\Delta^1$ -menthen-3-one, b. p.  $235^{\circ}$ , carvotanacetone, b. p.  $228-229^{\circ}$ , 1-methyl-2-isopropyl- $\Delta^1$ -cyclohexen-3-one, b. p.  $216-217^{\circ}$ , and  $\Delta^4$ -menthen-3-one, b. p.  $211^{\circ}$ , and (iii) the fall in the b. p. by the conversion of unsaturated ketones of the type -COMe into saturated ketones of the type  $\text{C}_6\text{H}_{11}\cdot\text{COMe}$  is about  $19^{\circ}$ , and is therefore distinctly greater than the fall, about  $3-4^{\circ}$ , in the b. p. caused by the conversion of - $\text{CH}_2\cdot\text{COMe}$  into  $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{COMe}$ .

1:4-Dimethyl- $\Delta^6$ -cyclohexen-2-oneoxime,  $\text{NOH}\cdot\text{C}\langle\begin{smallmatrix} \text{CMe}=\text{CH} \\ \text{CH}_2\cdot\text{CHMe} \end{smallmatrix}\rangle\text{CH}_2$ , m. p.  $92-93^{\circ}$ , and another substance, m. p.  $163^{\circ}$ , which is apparently an isomeride, are obtained by warming the nitrosochloride of 1:4-dimethyl- $\Delta^1$ -cyclohexene with sodium acetate in glacial acetic acid. By hydrolysis, the former yields 1:4-dimethyl- $\Delta^1$ -cyclohexen-2-one b. p.  $189-190^{\circ}$ ,  $D^{20}_D$   $0.938$ ,  $n^{20}_D$   $1.4753$  (semicarbazone, m. p.  $165^{\circ}$ ), which is oxidised to *p*-xylenol by ferric chloride and glacial acetic acid.

By reduction of Paal's method, 1:4-dimethyl- $\Delta^6$ -cyclohexen-2-one yields 1:4-dimethylcyclohexan-2-one, b. p.  $178^{\circ}$ ,  $D^{20}_D$   $0.9025$ ,  $n^{20}_D$   $1.4446$  (oxime, m. p.  $108-109^{\circ}$ , semicarbazone, m. p.  $175-176^{\circ}$ ), which is also obtained by warming 1:4-dimethylcyclohexan-1:2-diol with dilute sulphuric acid. The saturated ketone and its oxime and semicarbazone have been described, frequently but erroneously, in the literature. By oxidation with chromic and dilute sulphuric acids, it is converted into  $\delta$ -acetyl- $\beta$ -methylvaleric acid (semicarbazone, m. p.  $146-147^{\circ}$ ), which in turn is oxidised to  $\beta$ -methyladipic acid by sodium hypobromite.

By reactions similar to the preceding, tetrahydro-*m*-xylene nitrosochloride is converted successively into 1:3-dimethyl- $\Delta^3$ -cyclohexen-4-oneoxime, 1:3-dimethyl- $\Delta^2$ -cyclohexen-4-one (semicarbazone, m. p. 194—195°), and 1:3-dimethylcyclohexan-4-one (this vol., i, 278).

1-methylcyclohexan-5-one, b. p. 181.5—182°,  $D^{19}_D$  0.895,  $n_D$  1.4425 (semicarbazone, m. p. 201°), and 1:3-dimethylcyclohexan-2-one, b. p. 174.5°,  $D^{20}_D$  0.9140,  $n_D$  1.4476 (oxime, m. p. 114—115°, semicarbazone, m. p. 176—177°), have been prepared and their physical constants and those of the oximes and semicarbazones compared with the values recorded by other investigators.

[With Louis AUGSPURGER.]—By reactions similar to the preceding, 1-methyl-4-ethyl- $\Delta^3$ -cyclohexene nitrosochloride has been converted successively into 1-methyl-4-ethyl- $\Delta^3$ -cyclohexen-5-oneoxime, m. p. 59—66°, 1-methyl-4-ethyl- $\Delta^3$ -cyclohexen-5-one, b. p. 203—204°,  $D^{19}_D$  0.9310,  $n_D$  1.4759 (semicarbazone, m. p. 152—153°), and 1-methyl-4-ethylcyclohexan-5-one, b. p. 197°,  $D^{20}_D$  0.9000,  $n_D$  1.4485 (semicarbazone, m. p. 178—181°, oxime, m. p. 80°). By oxidation with chromic acid the last substance yields a ketonic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COEt}$  (semicarbazone, m. p. 145°).

1-iso-Propylcyclohexan-4-one, b. p. 214—214.5°,  $D^{19}_D$  0.9175,  $n_D^{19}$  1.4561, (dibenzylidene compound, m. p. 105°), is obtained by the reduction of 1-isopropyl- $\Delta^1$ -cyclohexen-4-one (A., 1908, i, 424) by Pail's method. 1-Methyl-3-isopropyl- $\Delta^6$ -cyclohexen-5-one, b. p. 244° (decomp.),  $D^{21}_D$  0.9340,  $n_D^{21}$  1.4865 (semicarbazone, m. p. 167°), is reduced by Pail's method to 1-methyl-3-isopropylcyclohexan-5-one, b. p. 221—223°,  $D^{20}_D$  0.8965,  $n_D$  1.4541.

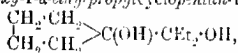
[With RUD. MÜLLER and FR. HENJES.]—The low b. p., 212°, of  $\Delta^4$ -menthen-3-one, in comparison with those of the isomerides,  $\Delta^1$ -menthen-3-one, 235—237°, carvenone, 232—233°, and carvotanacetone, 228—229°, led the authors to the opinion that an error must have been made either in the b. p. or in the constitution (compare Auwers, A., 1909, i, 592). It is now shown that no error had been committed. *i*- $\Delta^4$ -Menthen-3-one, prepared from *i*-menthene, has b. p. 212—213°,  $D^{20}_D$  0.9165,  $n_D$  1.4726, whilst *l*- $\Delta^4$ -menthen-3-one, prepared from menthol, is a yellow liquid having b. p. 211—212°,  $D^{18}_D$  0.919,  $n_D$  1.4729, and  $[\alpha]^{25}_D$  - 67.46° in methyl alcohol. The active substance forms a semicarbazone, m. p. 170—171°, and a dibenzylidene derivative, yellow needles, m. p. 140—141°,  $[\alpha]^{25}_D$  - 58.41° in chloroform. The constitution of the active menthenone is proved by its reduction to *l*-menthone by Pail's method, and ultimately to *l*-menthol by sodium and alcohol. The constitution of the *i*-menthenone has been proved by the synthesis of the ketone from 1-methylcyclohexan-4-one and magnesium isopropyl iodide, the resulting alcohol being dehydrated by dilute sulphuric acid, and the 1-methyl-4-isopropyl- $\Delta^3$ -cyclohexene being converted through the nitrosochloride into the menthenoneoxime. The low b. p. of  $\Delta^4$ -menthen-3-one, therefore, must be due to the position of the isopropyl group between the carbonyl group and the ethylenic group (compare above).

[With FR. HENJES.]—Since little is accurately known of the derivatives of *i*-menthone, a large quantity of this ketone has been prepared by reducing  $\Delta^1$ -menthen-3-one by Pail's method. It has b. p. 210°.

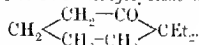
$D^{20}_D$  0.8975,  $n_D$  1.4521, and forms a semicarbazone, m. p. 212°, oxime, m. p. 79—80° (benzoyl derivative, m. p. 69—70°), *isooxime*, m. p. 87—88°, hydrochlorobenzylidene derivative, m. p. 119—120°, and yields a mixture of menthols by reduction. The reduction of *i*-menthoneoxime yields *i*-menthylamine, b. p. 208°, which forms a hydrochloride, m. p. above 250°, carbamide, m. p. 151—152°, phenylmenthylcarbamide, m. p. 135—136°, phenylthiocarbamide, m. p. 136—137°, and benzylidene compound, m. p. 141—142°. C. S.

**Pinacolin Transformation.** II. **Asymmetric Cyclic and Acyclic Pinacones and Their Transformation Products.** HANS MEERWEIN (*Annalen*, 1913, 396, 200—263. Compare A., 1910, i, 836).—A thorough examination of the reaction whereby 1-isopropylcyclopentane-1- $\alpha$ -diol is converted into 1:1-dimethylcyclohexan-2-one and of analogous reactions has led to the following important generalisations in connexion with the pinacolin transformation: (1) the pinacolin transformation is a true, intramolecular, atomic rearrangement; intermediate products cannot be isolated; (2) the course of the transformation is conditioned by different factors depending on the structure of the pinacone. In symmetric pinacones of the type  $\text{CRR}(\text{OH})\cdot\text{CRR}'\text{OH}$ , the transformation depends only on the relative ease of mobility of the groups R and R', whilst in asymmetric pinacones,  $\text{CR}_2(\text{OH})\cdot\text{CR}'_2\text{OH}$ , the stability of the hydroxyl groups is the determining factor; (3) by a study of the pinacolin transformation, it is possible, not only experimentally to ascertain the different stabilities (that is, the strength of their attachment to the carbon atoms) of the hydroxyl groups in asymmetric pinacones, but also, since such stability is determined mainly by the stabilities of the radicals attached to the same carbon atom, the relative strengths of the attachment of these radicals.

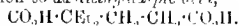
[With HANS PROBST.]—The interaction of methyl cyclopentan-1-ol-1-carboxylate and an excess (4—5 mols.) of magnesium ethyl bromide or magnesium phenyl bromide leads by the usual method to the formation of 1-hydroxy-1- $\alpha$ -ethylpropylcyclopentan-1-ol,



m. p. 39.5°, b. p. 136°/25 mm., and 1- $\alpha$ -hydroxybenzylcyclopentan-1-ol,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{C}(\text{OH})\cdot\text{CPh}_2\text{OH}$ , m. p. 125°, colourless prisms, respectively. The former is converted by concentrated sulphuric acid at -10° into a mixture of 1:1-diethylcyclohexan-2-one,



b. p. 93°/15 mm.,  $D^{20}_D$  0.9236,  $n_D$  1.4621 (the constitution of which is proved by its oxidation to *aa*-diethylglutic acid),



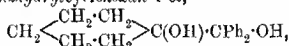
m. p. 91—92°, by nearly boiling 30% nitric acid, and 1-propionyl-1-ethylcyclopentane,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \quad | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} > \text{CET}\cdot\text{COEt}$ , b. p. 86°/16 mm.,  $D^{20}_D$  0.9104,  $n_D$  1.4525, which is oxidised to 1-ethylcyclopentan-1-carboxylic acid,

m. p.  $-8^{\circ}$ , b. p.  $132^{\circ}/18$  mm., by nearly boiling 40% nitric acid. The separation of the mixture is readily effected by means of the semicarbazones, the *semicarbazone*, m. p.  $202-203^{\circ}$ , rhombic leaflets, of the cyclohexane derivative being sparingly soluble in alcohol or other solvents, whilst the *semicarbazone*, m. p.  $148.5^{\circ}$ , slender needles, of the cyclopentane derivative is easily soluble.

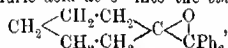
The pinacolin transformation of 1- $\alpha$ -hydroxybenzhydrylcyclopentan-1-ol by cold concentrated sulphuric acid yields only 1:1-diphenylcyclohexan-2-one, m. p.  $99^{\circ}$ , stout needles (*semicarbazone*, m. p.  $240^{\circ}$ ), by the oxidation of which by chromic and acetic acids benzophenone is produced.

[With F. KREMERS.]—The product of the pinacolin transformation of 1-isopropylcyclohexane-1- $\alpha$ -diol contains about 33% of 1:1-dimethylcycloheptan-2-one (*semicarbazone*, m. p.  $169^{\circ}$ ) in addition to the 1-acetyl-1-methylcyclohexane described by Tarboureitch.

1- $\alpha$ -Hydroxybenzhydrylcyclohexan-1-ol,



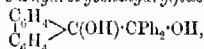
m. p.  $130^{\circ}$ , stout prisms, prepared from methylcyclohexan-1-ol-1-carboxylate and magnesium phenyl bromide, is transformed by concentrated sulphuric acid at  $0^{\circ}$  into the ethylene oxide,



m. p.  $92-94^{\circ}$ , rhombic prisms, which does not react with semicarbazide and is oxidised to benzophenone, glutaric and adipic acids by chromic and acetic acids.

[With F. KREMERS and R. SPLITTEGARD.]—Ethyl 9-hydroxyfluorene-9-carboxylate reacts in the usual manner with an excess, 7–8 mols., of magnesium methyl iodide, magnesium ethyl bromide, or magnesium phenyl bromide to form, ultimately, 9- $\beta$ -hydroxyisopropylfluorene,  $\text{C}_{16}\text{H}_{14} > \text{C}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{OH}$ , m. p.  $101^{\circ}$ , large, colourless needles.

9-hydroxydiethylmethylfluorene,  $\text{C}_{16}\text{H}_{14} > \text{C}(\text{OH}) \cdot \text{CEt}_2 \cdot \text{OH}$ , m. p.  $106^{\circ}$ , colourless needles, and 9- $\alpha$ -hydroxybenzhydrylfluorene,



m. p.  $160-162^{\circ}$ , slender needles, respectively. By cold concentrated sulphuric acid the first is transformed into 9-acetyl-9-methylfluorene,  $\text{C}_{16}\text{H}_{14} > \text{CMe} \cdot \text{COMe}$ , m. p.  $89^{\circ}$ , b. p.  $181^{\circ}/18$  mm. (*semicarbazone*, m. p.  $254-256^{\circ}$ ), the second into 9-propionyl-9-ethylfluorene, m. p.  $5^{\circ}$  (*semicarbazone*, m. p.  $236^{\circ}$ ), and the last, which is readily decomposed into benzophenone and fluorenone by 10% alcoholic potassium hydroxide,

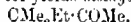
into 9:9-diphenylphenanthrone,  $\text{C}_{18}\text{H}_{14} \cdot \text{CPh}_2 \cdot \text{CO}$ , m. p.  $197^{\circ}$ , rhombic prisms.

The constitution of 9-acetyl-9-methylfluorene is proved by its decomposition into 9-methylfluorene and acetic acid by alcoholic potassium hydroxide, and by its oxidation to 9-methylfluorene-9-carboxylic acid,

m. p. 166°, glistening leaflets, by 10% sodium hypobromite. 9:9-Diphenyldiphenylmethane is identical with the substance described as  $\beta$ -diphenyldiphenylene-ethylene oxide by Werner and Grob, but that it has the constitution denoted by its name is proved by the fact that it yields the acid,  $\text{CHPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , by heating with alcoholic potassium hydroxide. Similarly, the pinacolins obtained by Zincke and Tropp from a series of pinacones prepared from phenanthraquinone and magnesium alkyl haloids, and regarded by them as  $\alpha$ -pinacolins ( $\beta$ -dialkyldiphenylene-ethylene oxides), are probably 9:9-dialkyldiphenylmethanes, since the methyl compound (9:9-dimethyldiphenylmethane), for example, is converted into 2-isopropylidiphenyl-2'-carboxylic acid,  $\text{CHMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. 104—106°, by potassium hydroxide at 220—240°.

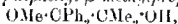
[With R. SPLITTEGARR.]—Acyclic, asymmetric pinacones have been prepared as similar as possible in structure to the preceding cyclic pinacones. Methyl  $\alpha$ -hydroxyisobutyrate reacts with magnesium ethyl or phenyl bromide to form, ultimately,  $\beta$ -methyl- $\gamma$ -ethylamylene  $\beta$ -glycol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{Cet}_2\cdot\text{OH}$ , b. p. 99—101°/19 mm., and  $\alpha\alpha$ -diphenyl- $\beta$ -methylpropylene glycol,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CMe}_2\cdot\text{OH}$ , m. p. 91°, respectively.  $\beta$ -Dimethylamylene  $\beta$ -glycol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CMeEt}\cdot\text{OH}$ , b. p. 94—95°/21 mm., is prepared from methyl methylethylglycolate, b. p. 151·6—152° (the ethyl ester has b. p. 162°, and the acid itself has b. p. 133—134°/16 mm.), and magnesium methyl iodide.

$\beta$ -Methyl- $\gamma$ -ethylamylene  $\beta$ -glycol is transformed by concentrated sulphuric acid into ethyl tert.-amyl ketone,  $\text{CMe}_2\text{Et}\cdot\text{COEt}$ , b. p. 150·5—152°,  $D^{20}_D$  0·8298 (semicarbazone, m. p. 98°), the constitution of which is proved by its oxidation to  $\alpha\alpha$ -dimethylbutyric acid by aqueous sodium hypobromite. By the pinacolin transformation,  $\beta$ -dimethylamylene  $\beta$ -glycol yields methyl tert.-amyl ketone,



b. p. 130·6°,  $D^{20}_D$  0·8243 (semicarbazone, m. p. 136—138°), which also yields  $\alpha\alpha$ -dimethylbutyric acid by oxidation.  $\alpha\alpha$ -Diphenyl- $\beta$ -methylpropylene- $\beta$ -glycol is transformed by cold concentrated sulphuric acid into methyl  $\alpha\alpha$ -diphenylethyl ketone, m. p. 41°, which is oxidised to  $\alpha\alpha$ -diphenylpropionic acid by sodium hypobromite.

[With F. KREMERS.]—Bromodiphenylacetic acid,  $\text{CPh}_2\text{Br}\cdot\text{CO}_2\text{H}$ , m. p. 133—134°, prepared from benzoic acid and hydrogen bromide in glacial acetic acid at 0°, is readily converted by methyl alcohol and sulphuric acid into methyl methoxydiphenylacetate, b. p. 191—196 mm., m. p. 29°, which reacts with magnesium methyl iodide to form, ultimately,  $\gamma$ -methoxy- $\gamma\gamma$ -diphenyl- $\beta$ -methylpropane  $\beta$  ol,



m. p. 45—47°, b. p. 181—182°/16 mm.; the latter is converted by cold concentrated sulphuric acid into methyl  $\alpha\alpha$ -diphenylethyl ketone, not into  $\omega$ -phenyl- $\omega\omega$ -dimethylacetophenone.

[By the AUTHOR.]—The various explanations of the pinacolin transformation are stated and criticised. The most widely accepted theory assumes the intermediate formation of ethylene oxides, but is not in agreement with observations of the author, Tiffeneau, Montagne, and others. The formation of tangible, intermediate products has not been observed, the transformation occurring by loss of water and the

migration of one group. The water must be eliminated before the migration occurs, because *s*- and *as*-diphenylmethylpropylene glycol yield the same pinacolin,  $\text{CPh}_2\text{MeCOMe}$ , and *s*- and *as*-dimethyldiethylethylene glycol also produce the same pinacolin,  $\text{CMe}_2\text{Et}(\text{C})\text{Et}$ . If these changes are explained by an interchange in position of a hydroxyl and an alkyl or aryl group and subsequent elimination of water, the author claims that sometimes one group, sometimes another, changes position with the hydroxyl group without any regularity or obvious reason.

The first step in the transformation, therefore, is  
 $\text{OH}\cdot\text{CR}_2\cdot\text{CR}_2\cdot\text{OH} \rightarrow \cdot\text{CR}_2\cdot\text{CR}_2\cdot\text{O}\cdot$

The complex then changes to a stable state, either  $\text{O} \begin{smallmatrix} \text{CR}_2 \\ \diagup \\ \text{CR}_2 \end{smallmatrix}$  which is quite exceptional, or  $\text{CR}_2\cdot\text{COR}$ . Symmetric pinacones,  $\text{OH}\cdot\text{CRR}'\cdot\text{CRR}'\cdot\text{OH}$ ,

contain hydroxyl groups of like function, and therefore yield, by loss of water, the complex  $\cdot\text{CRR}'\cdot\text{CRR}'\cdot\text{O}\cdot$ . The final state of this complex depends on the relative mobilities of R and R'; in general, the methyl group migrates more readily than its homologues, aliphatic groups less readily than aromatic, and substituted aromatic groups more readily than the phenyl radicle. In asymmetric pinacones,  $\text{OH}\cdot\text{CR}_2\cdot\text{CR}_2'\cdot\text{OH}$ , the hydroxyl groups are not of similar function, and, therefore, the first step of the pinacolin transformation may be the formation of  $\cdot\text{CR}_2\cdot\text{CR}_2'\cdot\text{O}\cdot$  or  $\cdot\text{CR}_2'\cdot\text{CR}_2\cdot\text{O}\cdot$  or both, the actual course being determined by the relative stabilities of the two hydroxyl groups. When the stabilities are about equal, two products are obtained, as, for example, 1:1-diethylcyclohexan-2-one and 1-propionyl-1-ethylcyclopentane from 1-hydroxydiethylmethylcyclopentan-1-ol. Hitherto, nothing has been known of the influence of alkyl groups on the stability of hydroxyl groups; since *as*-dimethyldiethylethylene glycol is transformed into ethyl tert.-amyl ketone, it appears that the hydroxyl group in the neighbourhood of the heavier alkyl group has the greater stability. C. S.

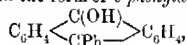
Syntheses by means of Sodamide. ALBIN HALLER and ÉDOUARD BAUER (*Ann. Chim. Phys.*, 1913, [viii], 28, 373—414).—A résumé of information on this subject, referring principally to the results recorded in the following Abstracts: 1909, i, 108, 654; 1911, i, 726, and 1912, i, 270. T. A. H.

A Fourth Modification of Benzophenone. WALTER A. WARR (*Chem. Zentr.*, 1913, i, 813—814; from *Öfvers. Finska Vetens. Soc. Förhandl.*, 1911, 54, A, 10. Compare A., 1912, ii, 1044).—When benzophenone is melted in a narrow, thin-walled glass tube at 50°, and then plunged into a carbon dioxide-ether mixture, a vitreous mass is obtained which develops spherulitic groups of fibrous crystals at  $-60^\circ$  to  $-65^\circ$  which melt at  $-51^\circ$ . Tammann observed that the speed of crystallisation of stable benzophenone (I) below  $-40^\circ$  is so small that this form cannot be produced at such low temperatures at all. The new labile modification (IV) can therefore melt without

passing into the stable form. The other modifications are Tammann's (II) with m. p. 45—48° and Zincke's (II), m. p. 26°. J. C. W.

**Anthracene. III. Derivatives of Anthrone.** KURT H. MEYER and ALBERT SANDER (*Annalen*, 1913, 396, 133—151).—The influence of substituents in position 9 on the desmotropy of anthrone has been further examined. Anthrone itself, even in solution, exists chiefly in the ketonic modification; anthraquinol and its methyl ether, however, are mainly enolic.

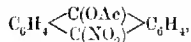
On account of its non-fluorescence, insolubility in cold alkalis, and indifference to alcoholic bromine, 9-phenylanthrone exists in the ketonic form. By solution in hot alkali and precipitation by acid in the cold, it is obtained in the form of 9-phenylanthranol,



which is sulphur-yellow and yields intensely fluorescent solutions; by keeping or by crystallisation, the anthranol reverts to the anthrone.

The equilibrium of the two modifications of this substance (and also of the following substances) in solution has been determined as follows. An alcoholic solution, about 0.1% at the ordinary temperature is intensely illuminated by an iron arc and is titrated with  $N_{10}$ -alcoholic bromine. Since only the enolic form reacts with bromine and is fluorescent, the disappearance of the fluorescence furnishes a sharp end-point. The same result is attained by starting with the anthrone or the anthranol, provided that the solution has been kept for a sufficiently long time. By this method it is shown that glacial acetic acid favours the formation of the ketonic modification, that all anthrone derivatives are immediately converted into anthranols by pyridine, that equilibrium is not attained in benzene or chloroform even after prolonged boiling, and that the velocity of transformation in alcohol is very much increased by the addition of concentrated hydrochloric acid and, still more, of sodium acetate.

9-Nitroanthrone, which is readily obtained by the nitration of anthrone in glacial acetic acid by nitric acid, D 1.5, at 60°, is converted into 9-nitroanthranol (Mei-enheimer's *aci*-nitroanthrone) by solution in hot alkali and precipitation in the cold by acids. After equilibrium has been established in alcohol, the solution contains 97% of the ketonic form. The end-point is readily detected, since 9-nitroanthranol is yellow, and 9-nitroanthrone is colourless, in solution. 9-Nitroanthrone is converted into 9-nitroanthranyl acetate,



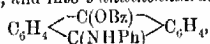
m. p. 182°, citron-yellow leaflets or needles, by acetyl chloride in cold pyridine, and into 9-nitroanthranyl benzoate, m. p. 238° (decomp.), amber-yellow prisms, by benzoyl chloride and pyridine on the water-bath.

9-Anilinoanthrone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH(NHPh)} \end{array} \text{C}_6\text{H}_4$ , m. p. 154—156°, reddening at 146°, faintly yellow needles, prepared from 9-bromoanthrone and aniline in boiling benzene, is converted by treatment



with alcoholic potassium hydroxide and subsequent acidification into 9-anilinoanthranol,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OH)} \\ \text{C(NHPh)} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p.  $155^\circ$ , reddish-brown crystals, which forms orange-red solutions with intense yellowish-green fluorescence. The alcoholic solution, after several days, contains about 80% of the anthranol. Both forms are converted into anthraquinol and aniline by boiling dilute acids and alcohol. 9-Anilino-

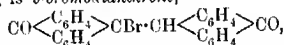
anthrone is converted into 9-anilinoanthrone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{C(NPh)} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p.  $123-124^\circ$ , red needles, by alcoholic potassium hydroxide and potassium ferriyanide, and into 9-anilinoanthranil benzoate,



m. p.  $226^\circ$ , yellow crystals, by benzoyl chloride and cold pyridine.

9- $\beta$ -Naphthylaminoanthrone, m. p.  $179-180^\circ$ , yellow needles, 9- $\beta$ -naphthylaminoanthranol, m. p.  $187-188^\circ$ , bluish-black needles, and 9- $\beta$ -naphthylaminoanthrone, m. p.  $167-168^\circ$ , dark red crystals, are prepared by methods similar to the preceding.

With the object of preparing 9-aminoanthrone, a cold solution of 9-bromoanthrone in dry benzene was saturated with ammonia. The product, however, is 9-bromoanthrone,



amber crystals, which, above its m. p.,  $187^\circ$ , or by boiling with xylene and copper powder, is converted into dianthrone. 9-Aminoanthrone in a very impure state is produced by reducing benzeneazoanthranol with zinc dust and alcoholic sodium hydroxide in an atmosphere of nitrogen. C. S.

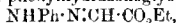
**Experiments on the Determination of the Constitution of Enolic Substances.** JOHANNES SCHEIDER and PAUL HEROLD (*Ber.*, 1913, 46, 1105-1110).—The authors have attempted to apply the use of ozone and subsequent decomposition of the ozonide formed for the determination of the constitution of enolic substances. The advantages claimed for the method are that operations can be carried out at low temperatures and that the addition of ozone, as far as is yet known, takes place without previous structural alteration of the substances investigated.

A solution of benzoylacetone in chloroform was treated with ozone and the ozonide subsequently decomposed by warm water. The cooled solution deposited an almost quantitative amount of benzoic acid, whilst the filtrate, when treated with phenylhydrazine, yielded methylglyoxalosazone, m. p.  $146^\circ$  (Harries and Türk, A., 1905, i, 413, give  $145^\circ$ ). Neither acetic acid nor carbon dioxide could be detected. Benzoylacetone appears therefore to be enolised according to the formula  $\text{OH} \cdot \text{CPh} \cdot \text{CH} \cdot \text{COMe}$ , which confirms the work of Smiedley (T., 1910, 97, 1486).

Oxalacetone, when similarly treated, gave a 93.5% yield of oxalic acid, from which it follows that enolisation must also have occurred to some extent towards the acetyl group. Although acetic acid could not

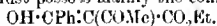
be detected, this is confirmed by the fact that phenylhydrazine did not yield pure methylglyoxalosazone.

The ozonide obtained in small quantity from ethyl acetoacetate, when decomposed by water, yielded with phenylhydrazine acetate a precipitate of pure ethyl phenylhydrazonoglyoxylate,



m. p.  $128^\circ$  (Reissert, A., 1895, i, 461, gives  $129^\circ$ ; v. Pechmann, 1896, i, 678, finds  $130\text{--}131^\circ$ ), from which the formula  $\text{OH}\cdot\text{CMe}:\text{CH}\cdot\text{CO}_2\text{Et}$  is deduced for the enolised ester.

Ethyl benzoylacetoacetate under similar treatment gave rise to benzoic acid and to the somewhat impure osazone of ethyl diketobutyrate,  $\text{CMe}(\text{N}_2\text{HPh})\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{CO}_2\text{Et}$ . Although the benzoic acid formed has not yet been estimated, the enolised form of ethyl benzoylacetoacetate must possess mainly the configuration



Diacetylbenzoylmethane, m. p.  $34^\circ$ , similarly yielded benzoic acid mixed with small quantities of a substance which could not be identified with certainty, whilst, after removal of benzoic acid, the bi-phenylhydrazone of triketopentane, m. p.  $155^\circ$  (Sachs and Barschall, A., 1901, i, 670, give  $156^\circ$ ), was isolated by means of phenylhydrazine. The authors conclude that the enolised form of diacetylbenzoylmethane consists mainly of the  $\alpha$ -form,  $\text{CPh}(\text{OH})=\text{C}\begin{smallmatrix} \text{COCH}_3 \\ \text{COCH}_3 \end{smallmatrix}$ , probably mixed

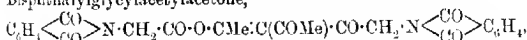
with small amounts of the  $\beta$ -variety,  $\text{CMe}(\text{OH})=\text{C}\begin{smallmatrix} \text{COCH}_3 \\ \text{CO}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}$ .

H. W.

**Phthalylglycyl Derivatives of Acetylacetone, Benzoylacetone, and Ethyl Cyanoacetate.** JOHANNES SCHEIBER [with K. KLOPPE and K. SCHNABEL] (*Ber.*, 1913, 46, 1100—1105).—The author has extended his work on the condensation of ethyl sodioacetoacetate with phthalylglycyl chloride (A., 1909, i, 390).

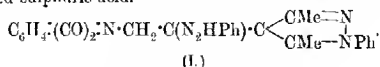
The sodium derivative of acetylacetone reacts readily with phthalylglycyl chloride in the presence of ether or benzene. The main product of the reaction is *bisphthalylglycylacetylacetone*, smaller quantities of *p*-*phthalylglycylacetylacetone* and *o*-*phthalylglycylacetylacetone* being also formed. The latter substance is, however, mainly formed when the silver derivative of acetylacetone is substituted for the sodium derivative. If the reaction is carried out in boiling benzene solution, *phthalylglycyl anhydride* is also obtained.

*Bisphthalylglycylacetylacetone*,

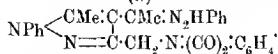


has a variable m. p., probably due to partial enolisation. Thus, a product, m. p.  $182^\circ$  (highest observed m. p.), after recrystallisation from glacial acetic acid had m. p.  $168^\circ$ . Cold sodium ethoxide converts it into *p*-*phthalylglycylacetylacetone*. With aniline it yields *phthalylglycylacetylacetone anilide*,  $\text{C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}(\text{COMe})\cdot\text{CMe}\cdot\text{N}\cdot\text{HPh}$ , yellow needles, m. p.  $172^\circ$ . Phenylhydrazine converts it into *phthalylglycylacetylacetonepyrazolephenylhydrazine* (formula I or II), lemon-yellow leaflets, m. p.  $193^\circ$ , the same substance being obtained from the

above anilide or from *C*-phthalylglycylacetylacetone. It is not decomposed by sodium hydroxide, does not reduce Fehling's solution, and gives a blue coloration with ferric chloride when dissolved in concentrated sulphuric acid.



(I.)



(II.)

*C*-Phthalylglycylacetylacetone, m. p. 124°, is soluble in aqueous sodium hydroxide without decomposition, and gives an immediate blood-red coloration with alcoholic ferric chloride.

*O*-Phthalylglycylacetylacetone, m. p. 107°, is insoluble in aqueous sodium hydroxide, and yields a red coloration with ferric chloride after some time. It is decomposed by a solution of phenylhydrazine in glacial acetic acid with formation of *phthalylglycylphenylhydrazide*,  $\text{C}_6\text{H}_4\cdot(\text{CO})_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ , m. p. 192°, which was also prepared from phthalylglycyl chloride and phenylhydrazine. When, however, the free acid was heated with phenylhydrazine in dilute acetic acid solution, the main product was anilinophthalimide,  $\text{C}_6\text{H}_4\cdot(\text{CO})_2\cdot\text{N}\cdot\text{NHPh}$ , m. p. 179°.

Phthalylglycyl anhydride,  $\text{C}_{20}\text{H}_{12}\text{O}_7\text{N}_2$ , white needles, m. p. 242°, is transformed by phenylhydrazine into phthalylglycylphenylhydrazide, and by aniline into phthalylglycylanilide, m. p. 231–232°. The latter substance was also obtained from phthalylglycyl chloride and aniline.

The action of phthalylglycyl chloride on the sodium derivative of benzoylacetone yields *bisphthalylglycylbenzoylacetone* and *O-phthalylglycylbenzoylacetone*. The former, m. p. 151°, gradually gives a red coloration with ferric chloride in alcoholic solution, and is converted by cold sodium alkoxide into *C-phthalylglycylbenzoylacetone*, m. p. 135°. The latter immediately gives an intense red coloration with ferric chloride.

*O*-Phthalylglycylbenzoylacetone, m. p. 147–148°, gives no coloration with ferric chloride, and is insoluble in sodium hydroxide. Phenylhydrazine eliminates the phthalylglycyl radical.

With ethyl sodiocyanoacetate, phthalylglycyl chloride yields practically solely *ethyl phthalylglycylcyanooacetate*, long needles, m. p. 149°. The ester is immediately soluble in alkali and alkali carbonate solutions, and gives an immediate intense red coloration with ferric chloride. An alcoholic solution of phenylhydrazine converts it into phthalylglycylphenylhydrazide. In glacial acetic acid solution at the ordinary temperature, however, phenylhydrazine converts it into a substance,  $\text{C}_{21}\text{H}_{20}\text{O}_7\text{N}_2$ , m. p. 156°, which is probably an additive product. It is soluble in sodium hydroxide, does not give Bilow's reaction, and reduces Fehling's solution in the cold. Concentrated sulphuric acid regenerates the ester.

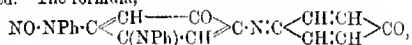
H. W.

**Action of Hydrochloric Acid on *p*-Benzoquinonesulphonic Acid.** ALPHONSE SEYEWETZ (*Compt. rend.*, 1913, 156, 901–903).—Concentrated hydrochloric acid acting on sodium *p*-benzoquinone-

sulphonate at temperatures below  $20^{\circ}$  yields after twelve hours a crystalline mass of *sodium chloroquinolsulphonate*,  $C_6H_4Cl(OH)_2 \cdot SO_3Na$ , white needles, soluble in water, instantly reducing silver nitrate. On oxidation it is converted into chloro-*p*-benzoquinonesulphonic acid.

If the reaction takes place at above  $20^{\circ}$ , the products are chloroquinol and 2:6-dibloroquinol. W. G.

**Action of Nitrous Acid on Dianilino-*p*-benzoquinoneanil.** CONSTANTIN I. ISTRATI and M. A. MIHAILESCU (*Bull. Acad. Sci. Roumaine*, 1912 3, 1, 25—29. Compare Istrati, A., 1903, i, 82).—When an excess of sodium nitrite is added to a solution of dianilino-*p*-benzoquinoneanil in cold glacial acetic acid, a number of products are obtained, of which three, m. p.  $209^{\circ}$ ,  $248^{\circ}$  and  $286^{\circ}$  respectively, have been isolated. The first of these separates from toluene in brilliant red leaflets. It is not attacked by boiling solutions of alkali hydroxides. It dissolves in concentrated sulphuric acid and in fuming nitric acid, but is precipitated unchanged when these solutions are diluted with water. It gives Liebermann's reaction, but the presence of a nitro-group could not be established. The formula,



is assigned to it, the dinitro-o-amine first formed undergoing partial rearrangement with the formation of the oxime of a substituted *p*-benzoquinoneimide, from which the *p*-benzoquinone is formed by elimination of hydroxylamine. H. W.

**Metaquinonoids.** RICHARD MEYER (*Ber.*, 1913, 46, 1220).—Stark and Garben (this vol., i, 361) relying on the earlier work of Meyer and Desamari (A., 1908, i, 658) included Liebermann and Dittler's tribromoresoquinone as a substance of metaquinonoid type. Later experiments of these authors, however, had already shown that the compound was a bimolecular keto-bromide,  $C_{12}H_2O_4Br_6$  (A., 1909, i, 241, 657). J. C. W.

**Preparation of Anthraquinone from Anthracene.** FARBWERKE vorm. MEISTER, LUCIUS & BREITING (D.R.-P. 256623).—Anthraquinone is obtained in 94—96% yield when an intimate mixture of anthracene, glass wool, or asbestos powder, and a metal or metallic oxide (such as zinc dust or lead oxide) is carefully treated with nitric acid fumes at  $75$ — $100^{\circ}$  for about nine hours; the temperature is then slowly raised to  $280^{\circ}$ , when the anthraquinone sublimes in long, yellow needles. F. M. G. M.

**Preparation of Chlorinated Anthraquinones and Anthracenes.** H. SCHULZ (Ber., 1913, 46, 1066—1069).—Starting from 1- and 2-chloroanthraquinone and from 1:5- and 1:8-dichloroanthraquinone, the author has prepared a number of the higher chlorinated anthraquinones by converting them into the corresponding chloroanthraquinonesulphonic acids and replacing the sulphonic acid with chlorine by treatment of the potassium salts of the sulphonic acids with chlorine in aqueous solution at  $100^{\circ}$ . The sulphonation

was carried out by heating the chloroanthraquinones with sulphuric acid containing 20% of anhydride for four hours at 150—160°, both alone and in the presence of mercurous sulphate. Although the position of the sulphonic acid groups has not been definitely established, it is assumed from the results of Schmidt (A., 1901, i, 256) and Hlinsky (A., 1904, i, 176) that in the presence of the mercurous salt the sulphonic acid group takes up the  $\alpha$ -position, whilst if no catalyst is employed the group enters the  $\beta$ -position.

With sulphuric acid alone monosulphonic acids are obtained. In the presence of mercurous sulphate 1-chloro- and the two dichloroanthraquinones yield disulphonic acids, whilst 2-chloroanthraquinone forms a monosulphonic acid. In addition to the disulphonic acid the 1:5-dichloro-compound also yields a monosulphonic acid.

The potassium salts of the chloroanthraquinonesulphonic acids are colourless or pale yellow, and are sparingly soluble in water.

The chloroanthraquinones are converted by reduction with zinc dust and ammonia into the corresponding chloroanthracenes, of which the monochloro-compounds form colourless, strongly, fluorescent leaflets or needles, whereas the di-, tri-, and tetra-chloro-derivatives crystallise in yellow needles.

In the following, (a) denotes sulphonation in the absence, (b) in the presence, of mercurous sulphate.

1-Chloroanthraquinone yields (a) 1-chloroanthraquinonesulphonic acid and (b) 1-chloroanthraquinone- $\alpha\alpha$ -disulphonic acid;  $\alpha\beta$ -dichloro (m. p. 166—168°) and  $\alpha\alpha$ -trichloroanthraquinones, m. p. 165—168°, which are reduced to  $\alpha\beta$ -dichloro (m. p. 130—135°) and  $\alpha\alpha$ -trichloroanthracene (m. p. 133—135°).

2-Chloroanthraquinone gives rise to (a) 2-chloroanthraquinone- $\beta$  and (b)  $\alpha$ -sulphonic acids;  $\beta\beta$ - and  $\alpha\beta$ -dichloroanthraquinones have m. p. 284—285° and 278—280° respectively, and yield  $\beta\beta$ - and  $\alpha\beta$ -dichloroanthracenes, m. p. 216° and 155—160°.

1:5-Dichloroanthraquinone gives rise to (a) 1:5-dichloroanthraquinone- $\beta$ -sulphonic acid and (b) 1:5-dichloroanthraquinone- $\alpha$ -sulphonic and  $\alpha\alpha$ -disulphonic acids; 1:5- $\beta$  (m. p. 230—235°) and 1:5- $\alpha$ -trichloroanthraquinone, m. p. 256°, and 1:5:4:8-tetrachloroanthraquinone, m. p. 339°; 1:5- $\beta$  trichloroanthracene has m. p. 170—175°, the 1:5:4:8-tetrachloro-compound, m. p. 275° or 285—286°, and the 1:5:  $\alpha$ -trichloro-compound, m. p. 270—275°.

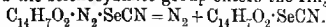
1:8-Dichloroanthracene yields (a) 1:8-dichloroanthraquinone- $\beta$ -sulphonic acid and 1:8-dichloroanthraquinone- $\alpha\alpha$ -disulphonic acid; 1:8- $\beta$  trichloroanthraquinone, m. p. 295—300°, and 1:8:  $\beta$  trichloroanthracene, m. p. 185—190°.

1-Chloroanthracene has m. p. 81—82°, 2-chloroanthracene, m. p. 215°, 1:5-dichloroanthracene, m. p. 185°, and 1:8-dichloroanthracene, m. p. 156°.

F. B.

Preparation of Selenocyanates of the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO (D.R.P. 256667).—When the anthraquinone diazoselenocyanates are carefully heated (preferably in the presence of copper or cuprous salts) nitrogen

is eliminated and the selenocyanate group enters the ring :



1. *Selenocyananthraquinone*, yellowish-red needles, m. p.  $249^\circ$ , is obtained when aminoanthraquinone (2.2 parts) is diazotised in concentrated sulphuric acid with nitrosyl sulphate, ice added, and the precipitated diazonium sulphate collected, dissolved in water, and treated with an aqueous solution of potassium selenocyanate (1.5 parts); the precipitated red *diazonanthraquinone selenocyanate* when warmed is converted into 1-selenocyananthraquinone, which is purified by crystallisation from nitrobenzene. *Potassium 1-selenocyananthraquinone-5-sulphonate* is prepared in a similar manner from sodium 1-aminoanthraquinone-5-sulphonate. F. M. G. M.

**Preparation of 2-Anthraquinone Sulphide.** IRMA ULLMANN-GOLDBERG (D.R.-P. 255591).—2-*Dianthraquinonyl sulphite*, orange-yellow prisms, m. p.  $275-276^\circ$ , is obtained when 2-chloroanthraquinone is boiled for six hours with an equal weight of potassium xanthate and 10 parts of amyl alcohol. F. M. G. M.

**Action of Colloidal Metallic Hydroxides on Hydroxyanthraquinones.** R. HALLER (*Farber-Zeit.*, 1912, 23, 489—492, 523—528).—A description of the preparation of colloidal solutions of aluminium, chromium, and ferric hydroxides, and of the complex salts:  $Al_2(SO_4)_2(OH)_2$ ,  $Al_2(SO_4)_2(OAc)_2$ ,  $Al_2(SO_4)(OAc)_4$ ,  $Al_2(SO_4)(OH)_2(OAc)_2$ ,

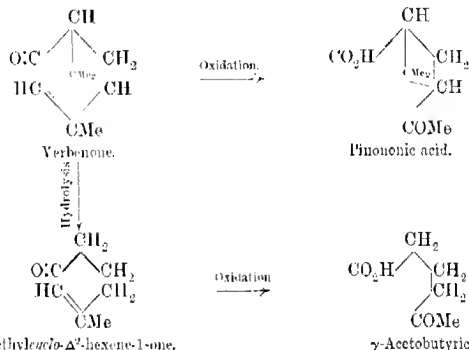
$Al_2(OAc)_6$ ,  $Al_2(OAc)_4(OH)_2$ , and  $Al_2(OAc)_2(OH)_4$ ; these were combined with alizarin, purpurin, anthrapurpurin, flavopurpurin, and alizarin-orange, and the physical and chemical properties of the compounds so obtained are comparatively tabulated with the normal iron, aluminium, and chromium salts.

The following properties were studied, absorption spectra, together with their behaviour in the presence of hydrochloric acid, ammonium hydroxide, calcium chloride, sodium chloride, sodium hydrogen phosphate, and absolute alcohol. F. M. G. M.

**Bupleurol or Dihydronerol. Constitution.** II. LUIGI FRANCESCONI and E. SERVACIOTTO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 148—154. Compare this vol., i, 283).—Reasons are advanced showing that bupleurol probably has the structure:  $CH_3M_2[CH_2]_3C(CH_3)CH_2CH_2OH$ . R. V. S.

**The Autoxidation of Turpentine.** ARNOLD BLUMANN and OTTO ZEITSCHSEL (*Ber.*, 1913, 46, 1178—1198).—On distilling a reified Greek turpentine in steam, the less volatile portions were found to respond to tests for aldehydes (compare Schiff, A., 1883, 141). An oil,  $C_{16}H_{34}O$ , was obtained on fractionation, but it was stable towards alkalis, did not readily yield an acid on oxidation, or a secondary alcohol with the Grignard reagent, neither would it undergo condensations. It was therefore considered to be a ketone with pseudo-aldehydic properties, like Wallach's isopropyl- $\Delta^2$ -hexenone (A., 1908, i, 425). Further investigations showed that it was unsaturated, and that it gave a saturated secondary alcohol with sodium

and moist ether, and a saturated ketone by Paal's reduction. It was completely identified with Kerschbaum's verbenone (A., 1900, i, 353), and its constitution was established, the chief evidence being that it gave pinononic acid on oxidation with permanganate (experiments by F. MEISTER), and that hydrolysis with dilute sulphuric acid resulted in the formation of acetone and a methylcyclohexenone, which gave  $\gamma$ -acetobutyric acid on oxidation.



Its rotation was stated by Kerschbaum to be  $+65^\circ$ , but it is really more by  $180^\circ$ . The *l*-modification was also obtained from French turpentine. Besides verbenone, the crude product contained alcoholic substances, evidence of the existence of verbenol being obtained, although the substance could not be completely purified.

The fact that the unsaturated linking of pinene is preserved after autoxidation seems contradictory, but it is assumed that the addition of water at this point precedes oxidation, and that after the latter process has occurred at the neighbouring  $-\text{CH}_2$ -group, the water is again eliminated.

From 900 grams of the less volatile constituents of Grecian turpentine which had been exposed to air for six months, 146 grams were collected at 105–107.5 mm. *d*-Verbenone,  $\text{C}_{10}\text{H}_{14}\text{O}$ , was separated from this by a neutral sulphite solution with sodium hydrogen carbonate (compare Tiemann, A., 1899, i, 247), or as the semicarbazone, in the form of a colourless oil, which soon became yellow in the light. It had h. p. 227–228°, or 100°/16 mm., m. p.  $6.5^\circ$ ,  $D^{20}_D 0.981$ ,  $D^{20}_D 0.9780$ ,  $[\alpha]_D +249.62^\circ$ ,  $[\alpha]_D$  in alcohol  $+229.60^\circ$ ,  $[\alpha]_D$  in benzene  $+215.70^\circ$ ,  $n^{20}_D 1.49928$ . It formed an *oxime*,  $\text{C}_{10}\text{H}_{14}\text{NOH}$ , m. p.  $115^\circ$ , was scarcely affected by hydrogen chloride in carbon disulphide or ether, or by acetic anhydride, but it absorbed hydrogen chloride with partial decomposition in glacial acetic acid. On reduction with sodium in moist ether, it yielded *dihydro-d-verbenol*,  $\text{C}_{10}\text{H}_{16}\text{O}$ , in silky needles with the celery-like smell of verbenone, m. p.  $58^\circ$ , b. p.  $218^\circ$ ,  $n_D +1.30$  (10% alcoholic solution). The *acetate*,  $D^{15}_D 0.9926$ ,  $n_D -0.50^\circ$  (25 mm.), and the *phthalate*,  $\text{C}_{18}\text{H}_{22}\text{O}_4$ , m. p. 127–129°, were prepared. On

oxidation it yielded *dihydro-d-verbenone*,  $C_{10}H_{16}O$ , which was also obtained by reduction of verbenone with colloidal palladium and hydrogen as an oil, b. p.  $222^{\circ}$ ,  $D^{15}_D$  0.9685,  $D^{20}_D$  0.9665,  $D^{25}_D$  0.9642,  $[\alpha]_D^{25} + 52.19^{\circ}$ ,  $n_D^{20}$  1.47535. The *semicarbazone*, m. p.  $220-221^{\circ}$ , the *oxime*, m. p.  $77-78^{\circ}$ , and the *benzylidene* compound, m. p.  $152-153^{\circ}$ , or  $103-104^{\circ}$  after three months, were obtained. Verbenone was also treated with magnesium methiodide, when the lowest fraction of the product was found to be an inactive hydrocarbon, *methylverbenene*,  $C_{11}H_{18}$ . The pure substance had b. p.  $49^{\circ}/8$  mm.,  $175-176^{\circ}/771$  mm.,  $D^{15}_D$  0.876,  $D^{20}_D$  0.872,  $n_D^{20}$  1.4969.

One kilogram of French turpentine was also exposed to air for three months, and 370 grams of less volatile products were fractionated, yielding 41.5 grams at  $90-100^{\circ}/12$  mm. By means of neutral sulphite, 18 grams of *l-verbenone* were obtained, having a lower rotation than the isomeride,  $[\alpha]_D^{25} - 126.84^{\circ}$ ,  $D^{15}_D$  0.980,  $n_D^{20}$  1.4994, and forming a *semicarbazone*, m. p.  $185-190^{\circ}$ . The *semicarbazone* from inactive verbenone had m. p.  $180-181^{\circ}$ .

The alcohol present in the residue which remained after shaking the high fraction with sulphite was isolated by means of benzoyl chloride in pyridine. The benzoate,  $D^{15}_D$  1.048, gave an oil on hydrolysis, which solidified in a freezing mixture to a mass of large leaflets. After pressing out the impurities the purified *d-verbenol*,  $C_{10}H_{16}O$ , had the constants, b. p.  $216-218^{\circ}$ , with elimination of water,  $D^{15}_D$  0.9742,  $D^{20}_D$  0.9722,  $D^{25}_D$  0.9702,  $[\alpha]_D^{25} + 132.30^{\circ}$ ,  $n_D^{20}$  1.4890. No solid derivatives could be obtained, but the alcohol gave verbenone with chromic acid, and pinonic acid with permanganate. When the crude or pure substance was heated with acetic anhydride, water was easily removed and *l-verbenone*,  $C_{10}H_{16}$ , was obtained, b. p.  $159-160^{\circ}$ ,  $D^{15}_D$  0.8852,  $D^{20}_D$  0.8822,  $n_D^{20}$  1.4902 (100 mm.),  $n_D^{20}$  1.4955. On the other hand, phosphoric oxide or zinc chloride yielded a hydrocarbon which was proved to be *p-cymene*, since it gave *p-hydroxyisopropylbenzoic acid* on warming with permanganate. The residue from *l-verbenone* was treated as above, but, although *l-verbenol* was found, it was still more difficult to purify it.

J. C. W.

**Synthetic  $\beta$ -Glucosides of the Terpene Alcohols.** JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, 49, 398-412).—The alcohols were shaken in ethereal solution with acetobromoglucose and silver carbonate, which were added in portions alternately. The glucosides were then obtained from the acetyl compounds thus produced by hydrolysis with barium hydroxide. The following substances were obtained: *d-Citronellol-tetra-acetyl-d-glucoside*,  $C_{22}H_{38}O_{11}$ , m. p.  $30^{\circ}$  (corr.), white needles from dilute alcohol. *d-Citronellol-d-glucoside*,  $C_{16}H_{26}O_6$ , a viscid syrup, with  $[\alpha]_D^{25} - 28.59^{\circ}$ ; it is hydrolysed by emulsin. *cycloHexanol-tetra-acetyl-d-glucoside*,  $C_{20}H_{30}O_{10}$ , m. p.  $119-120^{\circ}$  (corr.), and *cyclohexanol-d-glucoside*,  $C_{14}H_{22}O_6$ , m. p.  $133-135^{\circ}$  (corr.) (without water of crystallisation), with  $[\alpha]_D^{25} - 42.52^{\circ}$ . The substance with water of crystallisation has m. p.  $128.5-129.5^{\circ}$  (corr.); it is not very readily hydrolysed with emulsin. *Terpinol-3,2'-tetra-acetyl-d-glucoside*,  $C_{24}H_{36}O_{10}$ , m. p.  $114-116^{\circ}$ . *Terpinol-3,2'-d-glucoside*,  $C_{16}H_{24}O_6$ , sinters at  $50^{\circ}$ , m. p.  $90^{\circ}$ , with  $[\alpha]_D^{25} - 10.94^{\circ}$  when



anhydrous, and has a bitter taste. The form with  $11\text{H}_2\text{O}$  has m. p.  $80.5-82.5^\circ$  (corr.). The glucoside is not readily hydrolysed by emulsin. *Terpineol-35° tetra-acetyl-d-glucoside*,  $\text{C}_{24}\text{H}_{38}\text{O}_{10}$ , m. p.  $130-132^\circ$  (corr.). *Terpineol-55°-d-glucoside*,  $\text{C}_{16}\text{H}_{28}\text{O}_6$ , sinters at  $100^\circ$ , m. p.  $110^\circ$  (water free), with  $[\alpha]_D^{20} - 5.88^\circ$ ; it has a bitter taste; with water of crystallisation it melts at  $106-108^\circ$  (corr.); it is slowly hydrolysed by emulsin. *d-Dihydrocarveol-tetra acetyl-d-glucoside*,  $\text{C}_{24}\text{H}_{38}\text{O}_{10}$ , m. p.  $155-156^\circ$  (corr.). *d-Dihydrocarveol-d-glucoside*,  $\text{C}_{16}\text{H}_{28}\text{O}_6$ , m. p. (with water of crystallisation)  $164-165^\circ$  (corr.), with  $[\alpha]_D^{20} + 36.52^\circ$ . It is only sparingly soluble in water, and is hydrolysed readily by emulsin. *cis-Terpin-tetra-acetyl-d-monoglucoside*,  $\text{C}_{24}\text{H}_{38}\text{O}_{11}$ , m. p.  $129-139^\circ$  (corr.). *cis-Terpin-d-monoglucoside*,  $\text{C}_{16}\text{H}_{30}\text{O}_7$ , m. p.  $143-149^\circ$  (corr.), with  $[\alpha]_D^{20} - 11.03^\circ$ , is not readily hydrolysed by emulsin. S. B. S.

**Synthesis of Alkyl Glucosides by means of Emulsin.**  *$\beta$ -Phenylethyl Glucoside*, and  *$\beta$ -Cinnamyl Glucoside*. EMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, 156, 827-829; *J. Pharm. Chim.*, 1913, [vii], 7, 333-340).—The authors have prepared two other glucosides by their usual method (compare A., 1912, i, 672).

*$\beta$ -Phenylethyl glucoside*,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4$ , crystallises in colourless needles, having a bitter taste. It has  $[\alpha]_D - 23.92^\circ$ , and reduces Fehling's solution.

*$\beta$ -Cinnamyl glucoside*,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_4$ , crystallises in colourless needles,  $[\alpha]_D - 41.12^\circ$ , and having only a slight reducing action. Both of these glucosides are readily hydrolysed by emulsin in aqueous solution. W. G.

**Synthesis of Alkyl Galactosides by means of Emulsin.**  *$\beta$ -Methyl Galactoside* and  *$\beta$ -Allyl Galactoside*. EMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, 156, 1104-1106\*).—The two galactosides were prepared in the usual way by the action of emulsin on solutions of galactose in the respective alcohols. After evaporating off the excess of alcohol under reduced pressure, the unaltered galactose was destroyed by fermentation with bottom yeast in the presence of dextrose.

*$\beta$ -Allyl galactoside* crystallises in colorless needles,  $[\alpha]_D - 12.5^\circ$ , and, like the methyl galactoside, it is readily hydrolysed by emulsin in aqueous solution. W. G.

**Rhamnoxanthin from Rhamnus cathartica and Frangulin from Rhamnus frangula.** N. KRASOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 188-193. Compare A., 1909, ii, 174).—Examination of the two glucosides, rhamnoxanthin, and frangulin, and of their derivatives and products of hydrolysis indicates their identity. The name frangulin is suggested for retention. T. H. P.

**Preparation of the Active Principle of Apocynum.** F. BENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255537. Compare T., 1909, 95, 734).—The boiling carbon tetrachloride extract of the rhizome of *Apocynum cannabinum* furnished a compound, glistening prisms, m. p.  $135-140^\circ$ , with an extremely bitter taste, and contain-

\* and *J. Pharm. Chim.*, 1913, [vii], 7, 441-443.

ing C = 63.5% and H = 8.4% (compare Finnemore, T., 1908, 93, 1513; P., 1909, 25, 77). F. M. G. M.

The Blue Pigment from *Crenilabrus pavo*. RICHARD VON ZETZKE (*Monatsh.*, 1913, 34, 535—551. Compare A., 1902, i, 168).—A fuller account of the blue protein substance present in the fins, scales, and skin of *Crenilabrus pavo*. The fins, which are the best source of the substance, are extracted with acetone and ether successively, which remove a yellow substance, microscopic needles; this is easily soluble in chloroform, giving a solution which, on treatment with acetic anhydride and a drop of concentrated sulphuric acid, assumes a deep red colour, shortly changing to a bluish-green. After the above treatment, the fins are extracted with water, which dissolves out the coloured substance; this is purified by repeated precipitation by ammonium sulphate, and obtained as an amorphous solid. The optical properties of the substance have been re-investigated. The addition of magnesium sulphate, ammonium chloride, or sodium chloride causes the substance to separate slowly from its aqueous solution, and it is precipitated by the ordinary alkaloid reagents; its neutral solution coagulates at 75—77°, precipitating green flocks. The colour is only slowly bleached by hydrogen peroxide and hydrazine hydrate, but it is very sensitive towards acids, which evidently cause decomposition, as subsequent neutralisation fails to restore the original colour.

D. F. T.

Chlorophyll. XXI. Introduction of Magnesium into Chlorophyll Derivatives. RICHARD WILLSTÄTTER and LENNART FORSÉN (*Annalen*, 1913, 396, 180—193).—It has previously been shown that metals, such as copper, iron, and zinc, can easily be introduced into derivatives of chlorophyll, such as the phaeophorbides, phytychlorins, phytyrhodins, and the various porphyrins, producing substances which are characterised by their stability in acid or alkaline media. Also derivatives of the phytychlorins and the phytyrhodins have been prepared containing barium or potassium, and characterised by their instability towards acids. The magnesium derivatives are intermediate between these two extremes in their degree of stability. The present paper deals with the important problem of the methods whereby magnesium can be introduced into chlorophyll derivatives which do not contain a metallic constituent.

Two methods are described: heating the chlorophyll derivative with methyl-alcoholic potassium hydroxide and magnesium oxide under pressure, and secondly, treating it with an excess of ethereal magnesium methyl iodide.

Thus by heating phytychlorin-*a* (violet modification) with concentrated methyl-alcoholic potassium hydroxide and magnesium oxide in a silver autoclave at 180°, isolating the resulting potassium salt, and acidifying it with sodium dihydrogen phosphate, a new phyllin, called *eryanophyllin*,  $C_{55}H_{94}O_4N_4MgEt_2O$ , is obtained; it is a greenish-blue substance, characterised by the colour and fluorescence of its solutions and by its extraordinary instability, whereby the corresponding porphyrin is produced.

At 200° under similar conditions, phytochlorin-*a* is converted into a second phyllin, called *erythrophyllin*,  $C_{33}H_{34}O_4N_4Mg$ , which forms a red, fluorescent solution in ether. Still under the same conditions, phytochlorin-*a* at 220° is converted into phyllophyllin,  $C_{33}H_{34}O_2N_4Mg$ , which has previously been analysed only in the form of its salts on account of its instability. Phyllophyllin forms a bluish-red fluorescent ethereal solution, and readily loses its magnesium, yielding phylloporphyrin.

By treatment with magnesium methyl iodide (1 or 2 mols.) in ether, pheophytin-*a* yields precipitates containing magnesium and iodine, from which, however, the pheophytin is regenerated by treatment with water or other reagents. With an excess of magnesium methyl iodide (8 mols.), chlorophyll yields a substance from which unchanged chlorophyll is regenerated by treatment with sodium dihydrogen phosphate. In a similar manner the precipitate obtained from pheophytin-*a* and magnesium methyl iodide (8 mols.) yields, when rapidly treated with 10% sodium dihydrogen phosphate, pure chlorophyll-*a* identical with the substance prepared from natural sources.

In a similar manner, all porphyrins can be converted into the corresponding phyllins; thus phylloporphyrin methyl ester and magnesium methyl iodide in boiling ether yield a substance by the decomposition of which by sodium dihydrogen phosphate the methyl ester of phyllophyllin,  $C_{33}H_{36}O_2N_4Mg$ , is obtained in large, rhombic leaflets.

C. S.

[Action of Sodium Methoxide on Bilirubic Acid, Bilirubin, and Hemibilirubin.] OSKAR PILOTY (*Ber.*, 1913, 46, 1000—1001).— Polemical (compare Fischer and Röse, *A.*, 1912, i, 575; this vol., i, 382; also Piloty and Thannhauser, *A.*, 1912, i, 736, 925). Bilic and bilirubic acids are the same substance; further, isophanopyrrole-carboxylic acid is identical with the isophanopyrrolecarboxylic acid of Fischer and Bartholomäus (*A.*, 1912, i, 493), whilst dehydrobilic acid represents Fischer's xanthopyrrolecarboxylic acid or xanthobilirubic acid. The former name is to be preferred in each instance.

E. F. A.

The Action of Hydrogen Peroxide on Hippomelanin. JENNY ADLER-HERZMARK (*Biochem. Zeitsch.* 1913, 49, 130—136).— Hippomelanin, obtained from melanotic lymph glands of a horse, dissolves in hydrogen peroxide when treated by the method of Rana and Kiessner. About two-thirds of the nitrogen is thereby obtained in the form of ammonia. Part of the substance is converted into a product of the nature of melanic acid, which has been obtained from melanin by other methods. This product is slightly soluble in water, and is obtained in solution by the above-mentioned treatment in the form of an ammonium salt, from which the free acid can be precipitated by mineral acids, and from which an insoluble mercury salt can be obtained. No evidence could be obtained of the formation of guanidine or other basic organic substances.

S. F. S.

**Furoylformic Acid and Furylglycollic Acid.** EMIL FISCHER and FRITZ BRAUNS (*Ber.*, 1913, **46**, 892—896).—The similarity of pyromucic acid to benzoic acid extends even to the conversion through the chloride and cyanide into the corresponding ketonic acid.

Pyromucyl chloride, obtained from pyromucic acid and thionyl chloride, was treated in cooled ethereal solution with hydrogen cyanide and pyridine; the resultant oil was separated by distillation into a distillate of *furoyl cyanide*, hexagonal tablets, m. p. 25°, b. p. 32°/0.15 mm., and a residue of pyromucic anhydride. Furoyl cyanide is converted by dilute sodium hydroxide, or slowly by moist ethereal solution, largely into pyromucic acid. When kept with hydrochloric acid (D 1.19) for twenty-four hours, *furoylformic acid*,  $C_4H_3O \cdot CO \cdot CO_2H$ , is formed, which separates in colourless, microscopic needles, m. p. 94—95°, when the ethereal extract is treated with light petroleum; *silver* salt, amorphous; *phenylhydrazone*, m. p. near 151° (decomp.). The reduction of furoylformic acid by shaking with sodium amalgam and water yields *furylglycollic acid*,  $C_4H_3O \cdot CH(OH) \cdot CO_2H$ , m. p. indefinite at 114° (decomp.); the *calcium*, *silver*, and *lead* salts were prepared. Furoylformic acid thus shows marked similarity to benzoylformic acid.

D. F. T.

**Hydroxycatechin and Catechin-carboxylic Acids.** MAXIMILIAN NIERENSTEIN (*Annalen*, 1913, **396**, 191—200).—*Hydroxycatechin*

(annexed formula), m. p. 284—285° (decomp.), prepared by the reductive acetylation of catechone by acetic anhydride and zinc dust and hydrolysis of the product, crystallises in

yellow needles and forms a colourless *hexamethyl ether*, m. p. 102°, by treatment with diazomethane.

The yellow colour of hydroxycatechin, as also the red colour of 1:2:7:8-tetrahydroxydiphenylene oxide, is attributed to the influence of the hydroxyl group in the peri-position to the oxygen atom of the furan ring. Consequently, the presence of the more strongly acidic carboxyl group in the place of the peri-hydroxyl group should produce a still more intensely coloured catechin-carboxylic acid. The interaction of catechin, carbon tetrachloride, and aqueous potassium hydroxide, however, leads to the formation of a colourless *catechin-carboxylic acid*, m. p. 271—277° (decomp.), needles, which has the

constitution  $CO_2H \cdot C_6H_2(OH)_2 \cdot CH(OH) \cdot C_6H_2(OH)_2 \cdot \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} \cdot CH_2$ , since the *methyl catechin-carboxylate pentamethyl ether*,  $C_{20}H_{24}O_8$ , m. p. 92°, obtained from it by the action of diazomethane, yields hemipinic acid by oxidation with alkaline potassium permanganate.

The catechin-carboxylic acid has been resolved by means of its strychnine salts into the optically active components. 1-*Catechin-carboxylic acid* crystallises in small needles and has m. p. 270—273° (decomp.), and  $[\alpha]_D^{25} - 68.22^\circ$  in alcohol; the d-acid, small needles, has m. p. 273° (decomp.) and  $[\alpha]_D^{25} + 76.4^\circ$  in alcohol.

C. S.

**Adrenaline from the Whale.** ENWARD R. WEIDLEIN (*J. Ind. Eng. Chem.*, 1913, 4, 636—645).—The suprarenal glands of the whale are found to be about 500 times larger than those of sheep and fifty times larger than those obtained from cattle.

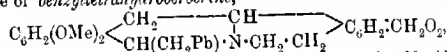
From the tabulated results of numerous experiments the conclusion is drawn that glands preserved in chloroform yield about 0.2% pure adrenaline (m. p.  $212^{\circ}$ ,  $[\alpha]_D^{25} - 52.00^{\circ}$ ) after preservation during six to nine months, the loss during purification amounting to 13.8%. Pure adrenaline gives a marked increase in blood pressure (as shown by curves) without a subsequent depressant action, this latter effect being considered to be due to impurities, proteins (such as lecithin and phosphates) present in the glands, and to decomposition products which are formed by oxidation on keeping for even a short time in aqueous solution.

The commercial adrenaline used for comparison gave the secondary depressant action until purified, although declared to be the best on the market.

The extraction and purification of the active suprarenal principle from the whale, cattle, sheep, and pigs is described, and it is demonstrated to be identical from each source. F. M. G. M.

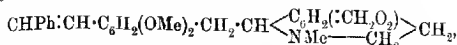
**Berberine.** MARTIN FREUND (*Annalen*, 1913, 397, 1—30).—A general discussion of the results of researches on dihydroberberine derivatives (compare following abstracts), one of the most important being the conversion of berberine into hydrastinine by a smooth and practicable method. C. S.

**Derivatives of Benzylidihydroberberine.** MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1913, 397, 30—52).—Benzylidihydroberberine (Freund and Beck, A., 1905, i, 151) yields the stannic chloride of benzyltetrahydroberberine,

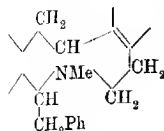


m. p.  $163\text{--}165^{\circ}$ , pale yellow, rhombic plates (*hydrochloride*, white needles; *sulphate*, decomp.  $227^{\circ}$ ; *nitrate*, decomp.  $175^{\circ}$ ), by reduction with stannous chloride and boiling 96% alcohol and hydrochloric acid, D 1.19. A second base is not formed, but when benzylidihydroberberine, dissolved in alcohol and 30% sulphuric acid, is reduced at a lead cathode at  $50\text{--}60^{\circ}$  (current-density at the cathode 0.06 ampere per sq. cm.), benzyltetrahydroberberine is produced, together with an isomeride,  $\text{C}_{27}\text{H}_{27}\text{O}_2\text{N}$ , m. p.  $126^{\circ}$ , a grey, crystalline powder, which is called *ψ-benzyltetrahydroberberine*. With methyl iodide at  $100^{\circ}$  it forms a *methiodide*, decomp.  $200^{\circ}$ , yellow powder, whilst *benzyltetrahydroberberine methiodide*, colourless, rhombic plates, has decomp.  $224^{\circ}$ . Both methiodides, by treatment with silver oxide and 50% alcohol and then with boiling potassium hydroxide, yield the same tertiary base, *de-benzyl-N-methyltetrahydroberberine*,  $\text{C}_{25}\text{H}_{25}\text{O}_2\text{N}$ , m. p.  $121\text{--}122.5^{\circ}$ , colourless, quadratic plates (*sulphate*, m. p.  $209\text{--}210^{\circ}$ ; *hydrochloride*, decomp.  $238\text{--}240^{\circ}$ ; *hydriodide*, m. p.  $193\text{--}194^{\circ}$ ). Since *de-benzyl-N-methyltetrahydroberberine* is converted into hydrastinine and 3:4-dimethoxy-2-styrylbenzaldehyde by oxidation with sodium dichromate in boiling acetic acid (this fissive oxidation is quite similar

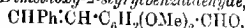
to that of landanoline described by Pyman [T., 1909, 95, 1267]), it receives the formula :



although, perhaps, a constitution containing the annexed skeleton is in better agreement with the facts that the de-base cannot be reduced and does not react with bromine.



3 : 4-Dimethoxy-2-styrylbenzaldehyde,

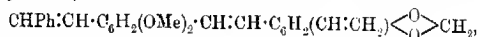


m. p. 71—74°, long, colourless needles, does not react with bromine in chloroform (steric hindrance ?), and forms an *oxime*, m. p.

125—140°, *phenylhydrazone*, m. p. 120—122°, yellow needles, *semicarbazone*, m. p. 190—192°, and *anil*, m. p. 107—109°; by reduction with sodium and warm alcohol, it is converted into 3 : 4-dimethoxy-2- $\beta$ -phenylethylbenzyl alcohol,  $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4(\text{OMe})_2 \cdot \text{CH}_2 \cdot \text{OH}$ , m. p. 96—98°, colourless needles.

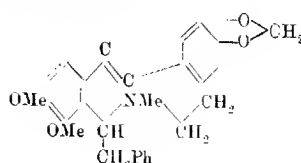
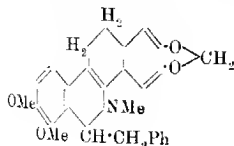
De-benzyl-N-methyltetrahydroberberine forms with methyl iodide at 100° a *methiodide*, m. p. 210°, yellow plates, which is converted, by successive treatment with silver oxide and 50% alcohol and with boiling potassium hydroxide, into de-benzyl-NN-dimethyltetrahydroberberine,  $\text{C}_{29}\text{H}_{31}\text{O}_4\text{N}$ , m. p. 93—94.5° (*sulphate*, m. p. 197°; *hydrochloride*, m. p. 238°), which cannot be reduced and is given the formula

$\text{CHPh} \cdot \text{CH} \cdot \text{C}_6\text{H}_4(\text{OMe})_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4(\text{CH}_2\text{O})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$ , because it yields 3 : 4-dimethoxy-2-styrylbenzaldehyde by fission oxidation. It forms a *methiodide*, m. p. 268°, which is decomposed and yields trimethylamine and 3 : 4-dimethoxy-3' : 4'-methylenedioxy-2-styryl-6-vinylstilbene,



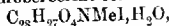
m. p. 120—122°, colourless needles, by the usual treatment.

Benzylidihydroberberine and methyl iodide at 100° yield a *substance*, decomp. 181°, which is not a *methiodide*, because it loses hydrogen iodide by treatment with alcoholic ammonia and yields a *substance*,  $\text{C}_{28}\text{H}_{27}\text{O}_4\text{N}$ , m. p. 187—188°, pale yellow, rhombic plates, which is called de-benzyl-N-methylidihydroberberine; the hydriodide of the latter is identical with the original additive compound. The constitution of de-benzyl-N-methylidihydroberberine has not been definitely settled; either of the annexed formulae may be possible, and serves to explain many of the following transformations of the substance, but objections can be raised against both :



m m 2

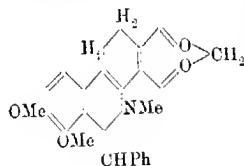
De-benzyl-*N*-methylidihydroberberine forms a *methiodide*,



decomp.  $167^\circ$ , reddish-yellow prisms, and is reduced by stannous chloride and boiling alcohol and hydrochloric acid, D 1.19, to the stannichloride of a substance,  $\text{C}_{28}\text{H}_{29}\text{O}_4\text{N}$ , m. p.  $162.5-164^\circ$ , colourless leaflets (*hydrochloride*, decomp. about  $215^\circ$ ; *sulphate*, decomp. above  $170^\circ$ ), which is called  $\alpha$ -hydro-de-benzyl-*N*-methylidihydroberberine. It is unchanged by bromine, iodine, or methyl iodide, and has only faintly basic properties. By reduction at a lead cathode in alcohol and 30% sulphuric acid at  $40-50^\circ$ , and with a cathodic current density of 0.075 ampere per sq. cm. and at 24 volts, de-benzyl-*N*-methylidihydroberberine is converted into a mixture of  $\alpha$ -hydro-de-benzyl-*N*-methylidihydroberberine and a substance,  $\text{C}_{28}\text{H}_{29}\text{O}_4\text{N}$ , m. p.  $134-136^\circ$ , microscopic plates, which is called  $\beta$ -hydro-de-benzyl-*N*-methylidihydroberberine. The mixture is readily separated, since only the  $\beta$  compound forms a *methiodide*. Analysis fails to determine whether the  $\alpha$ - and  $\beta$ -compounds are isomeric or whether one contains more hydrogen than the other. The preceding *methiodide* is converted, by treatment with silver oxide and subsequent boiling with an alkali, into  $\beta$ -hydro-de-benzyl-*NN*-dimethylidihydroberberine,  $\text{C}_{28}\text{H}_{31}\text{O}_4\text{N}$ , m. p.  $126^\circ$ , colourless needles, the *methiodide*, decomp.  $239^\circ$ , of which yields trimethylamine and a non-nitrogenous substance by the usual treatment.

The oxidation of de-benzyl-*N*-methylidihydroberberine by sodium dichromate and acetic acid at  $90^\circ$  produces, after dilution with water, a yellow (unexamined) solid and a green solution. Sodium carbonate precipitates from the latter *dehydro-de-benzyl-*N*-methylidihydroberberine*

(annexed formula), m. p.  $203-204^\circ$ , yellow prisms, which forms a *hydrochloride* and *sulphate*, decomp.  $229^\circ$ , but not a *methiodide*. By reduction with stannous chloride, alcohol, and concentrated hydrochloric acid, or at a lead cathode in alcohol and 3% sulphuric acid at  $40-50^\circ$ , *dehydro-de-benzyl-*N*-methylidihydroberberine* is converted into a substance,



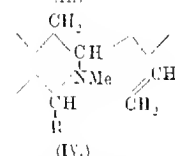
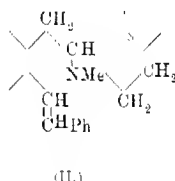
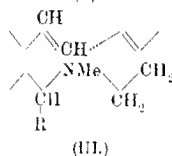
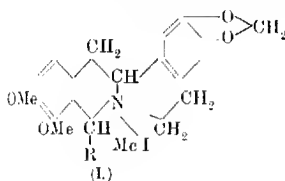
$\text{C}_{28}\text{H}_{27}\text{O}_4\text{N}$ , m. p.  $164-165^\circ$ , pale yellow, hexagonal plates, which appears to be isomeric with  $\alpha$ -hydro-de-benzyl-*N*-methylidihydroberberine.

Benzyltetrahydroberberine *methiodide* in aqueous alcoholic suspension is converted by silver chloride into the *methochloride*, decomp.  $226^\circ$ , rhombic plates, an aqueous solution of which on the water-bath is converted by 5% sodium amalgam into de-benzyl-*N*-methyltetrahydroberberine and *isohydro-de-benzyl-*N*-methyltetrahydroberberine*,  $\text{C}_{28}\text{H}_{31}\text{O}_4\text{N}$ , m. p.  $96-98^\circ$ , colourless plates (*hydriodide*, m. p.  $225^\circ$  [decomp.]).

**Methylidihydroberberine and its Derivatives.** MARTIN FRECH and HANS COMMESSMANN (*Annalen*, 1913, 397, 52-56).—Alkyl- or aryl-dihydroberberines react with methyl iodide to form the *hydriodides* of bases called de-alkyl- (or aryl-) *N*-methylidihydroberberines; by the

electrolytic method, each of the de-bases yields two reduction products,  $\alpha$  and  $\beta$ -hydro-de-alkyl-(or aryl)-*N*-methyl-dihydroberberines. Since these reduction products have similar properties, whether the alkyl or aryl group is methyl, ethyl, isopropyl, isobutyl, isoamyl, benzyl, or phenyl, the de-bases all have the same constitution, namely, that already given for the benzyl compound (Freund and Fleischer, preceding abstract).

By reduction, *R*-dihydroberberines each yield two stereoisomeric *R*-tetrahydroberberines, from which two stereoisomeric *R*-tetrahydroberberine methiodides (formula I) are obtained. (*R*-Tetrahydroberberines do not combine additively with iodides other than methyl iodide.) By treatment with silver oxide and subsequently with boiling alkali, the two methiodides yield one and the same de-base, which may have the constitution II, III, or IV. When *R* is  $\text{CH}_3\text{Ph}$ , the de-base has formula II (Freund and Fleischer, preceding abstract); when *R* is  $\text{Pr}^i$ , the de-base has constitution III (Freund and Fleischer, preceding abstract); when *R* is Me, Et,  $\text{CH}_2\text{Pr}^i$ ,  $\text{CH}_2\text{CH}_2\text{Pr}^i$ ,  $n\text{-C}_8\text{H}_{17}$ , or Ph, the de-base has formula IV.



*Methyltetrahydroberberine methiodide*,  $\text{C}_{22}\text{H}_{30}\text{O}_4\text{NI}$ , m. p. 263–264°, colourless prisms, is converted by the usual method into *de-methyl-N-methyltetrahydroberberine*,  $\text{C}_{16}\text{H}_{22}(\text{OMe})_2$ , m. p. 115–116°, colourless prisms (*hydrochloride*, m. p. 224–225° [decomp.]; *sulphate*, m. p. 211–212°; *nitrate*, m. p. 198–199° [decomp.]). The de-base does not yield hydrastinine by oxidation (*de-benzyl-N-methyltetrahydroberberine* is the only one that does), and forms a *methiodide*, m. p. 257° (decomp.), colourless needles.

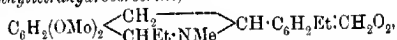
*Methyldihydroberberine* and methyl iodide form the *hydriodide*, m. p. 218° (decomp.), yellowish-green needles, of *de-methyl-N-methyl-dihydroberberine*,  $\text{C}_{20}\text{H}_{28}\text{O}_4\text{N}$ , m. p. 155°, yellow, irregular prisms (*sulphate*, m. p. 116° [decomp.]; *hydrochloride*, m. p. 104°). By electrolytic reduction at a lead cathode in alcohol and 20% sulphuric acid, the de-base is converted into  $\alpha$ -hydro-de-methyl-*N*-methyldihydroberberine,



$C_{22}H_{25}O_4N$ , m. p.  $146^\circ$  (sulphate, m. p.  $233^\circ$  [decomp.]; hydrochloride, m. p.  $155^\circ$  [decomp.]; nitrate, decomp.  $198^\circ$ ), and  $\beta$ -hydro-de-methyl-N-methylethyldihydroberberine,  $C_{23}H_{26}O_4N$ , m. p.  $215^\circ$  (sulphate, m. p.  $135$ — $138^\circ$  [decomp.]; hydrochloride, decomp.  $220^\circ$ ; nitrate, decomp.  $234^\circ$ ). The constitutions of the de-base and its reduction products are analogous to those of de-benzyl-N-methylethyldihydroberberine and its reduction products (Freund and Fleischer, preceding abstract). C. S.

**Ethyldihydroberberine and Its Derivatives.** MARTIN FREUND and HANNS COMMESSMANN (*Annalen*, 1913, 397, 57—69).—The reduction of ethyldihydroberberine at a lead cathode yields Freund and Mayer's ethyltetrahydroberberine, m. p.  $151^\circ$  (A., 1905, i, 657), and  $\psi$ -ethylethyltetrahydroberberine,  $C_{23}H_{26}O_4N$ , m. p.  $117$ — $119^\circ$ , faintly yellowish-green, irregular plates, which forms a sulphate, m. p.  $236^\circ$  (decomp.), hydrochloride, decomp.  $218^\circ$ , and nitrate, decomp.  $210^\circ$ .

Ethyltetrahydroberberine and methyl iodide at  $100^\circ$  yield the methiodide,  $C_{22}H_{25}O_4NMeI$ , m. p.  $228$ — $229^\circ$ , colourless needles, which is converted by the usual process into de-N-methyl- $\alpha$ -ethylethyltetrahydroberberine,  $C_6H_5(OMe)_2 \begin{matrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_2\text{O}_2 \\ \diagdown \quad \diagup \\ \text{CH} \text{Et} \cdot \text{NMe} \text{CH} \text{CH}_2 \end{matrix}$ , m. p.  $134^\circ$  (hydrochloride, decomp.  $220^\circ$ ; sulphate, decomp.  $239^\circ$ ; nitrate, decomp.  $152^\circ$ ). The de-base does not yield hydrastinine by oxidation, is also produced by the successive action of silver oxide and potassium hydroxide on  $\psi$ -ethylethyltetrahydroberberine methiodide, m. p.  $211^\circ$  (decomp.), and is reduced at a lead cathode in alcohol and 20% sulphuric acid to hydro-de-N-methylethyltetrahydroberberine,

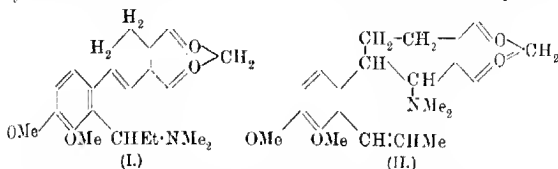


m. p.  $124$ — $125^\circ$  (sulphate, m. p.  $230^\circ$ ; hydrochloride, m. p.  $245^\circ$ ). De-N-methylethyltetrahydroberberine and methyl iodide at  $100^\circ$  form the methiodide,  $C_{22}H_{25}O_4NMeI$ , decomp.  $230^\circ$ , which is converted by silver oxide and potassium hydroxide in the usual manner into de-NN-dimethylethyltetrahydroberberine,  $C_{24}H_{28}O_4N$ , m. p.  $85$ — $86^\circ$ . The methiodide, m. p.  $208$ — $209^\circ$ , of the latter is decomposed into trimethylamine and 3:4-dimethoxy-3':4'-methylenedioxy-2-propenyl-6'-vinylstilbene,  $CH_3O \cdot CH \cdot C_6H_3(OMe)_2 \cdot CH \cdot C_6H_3(CH_2O_2) \cdot CH \cdot CH_3$ , m. p.  $82$ — $83^\circ$ , stout needles, by the usual treatment.

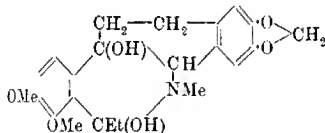
Ethyldihydroberberine and methyl iodide yield the hydriodide, m. p.  $210^\circ$  (decomp.), of de-N-methylethyldihydroberberine,  $C_{23}H_{26}O_4N$ , m. p.  $142$ — $143^\circ$ , softening at  $136$ — $137^\circ$ . The de-base forms a methiodide,  $C_{23}H_{25}O_4NMeI$ , m. p.  $250^\circ$  (decomp.), which yields by the usual method of decomposition de-NN-dimethylethyldihydroberberine,  $C_{24}H_{28}O_4N$ , m. p.  $115$ — $116^\circ$  (sulphate, m. p.  $191$ — $192^\circ$  [decomp.]; nitrate, decomp.  $168^\circ$ ; hydrochloride, decomp.  $163$ — $164^\circ$ ).

The reduction of de-N-methylethyldihydroberberine at a lead cathode in alcohol and 20% sulphuric acid yields a mixture of  $\alpha$ -hydro-de-N-methylethyldihydroberberine,  $C_{23}H_{26}O_4N$ , m. p.  $137^\circ$ , and  $\beta$ -hydro-de-N-methylethyldihydroberberine,  $C_{23}H_{26}O_4N$ , m. p.  $168^\circ$ . The  $\alpha$ -base forms a sulphate, decomp.  $188^\circ$ , hydrochloride, decomp.  $266^\circ$ , and nitrate, decomp.  $170^\circ$ , does not form a methiodide, and is converted

into *de-N*-methylethyldihydroberberine by bromine in chloroform and basification of the product. The  $\beta$ -base is unattacked by bromine, and forms a *sulphate*, decomp.  $107-108^\circ$ , *hydrochloride*, decomp.  $250^\circ$ , *nitrate*, decomp.  $185^\circ$ , and *methiodide*, m. p.  $245^\circ$  (decomp.). The decomposition of the last in the usual manner by silver oxide and potassium hydroxide yields a substance, m. p.  $104-120^\circ$ , which is probably a mixture of two isomeric  $\beta$ -hydro-*de-NN*-dimethylethyldihydroberberines (formulae I and II); the *methiodide* has decomp.  $230^\circ$ .



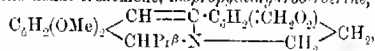
By oxidation with sodium dichromate and acetic acid at  $80^\circ$ , *de-N*-methylethyldihydroberberine yields a substance,  $C_{25}H_{27}O_6N$ , m. p.  $130^\circ$  (decomp.) (*hydrochloride*, m. p.  $225^\circ$ , colourless needles), which is called



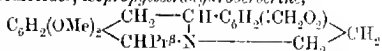
*oxy-de-N-methylethyldihydroberberine hydrate*, and possibly has the annexed constitution. This substance is also produced by

the oxidation of  $\alpha$ - or  $\beta$ -hydro-*de-N*-methylethyldihydroberberine; in addition, a second substance,  $C_{25}H_{25}O_6N$ , m. p.  $178^\circ$ , yellow crystals, is formed, which is provisionally named *iso-de-N-methylethyldihydroberberine*.  
C. S.

*iso*Propyldihydroberberine and its Derivatives. MARTIN FREUND and ROBERT LACHMANN (*Annalen*, 1913, 397, 70-84).—Berberine sulphate and ethereal magnesium *isopropyl* bromide react to form, after the usual treatment, *isopropylidihydroberberine*,



m. p.  $167-168^\circ$ , citron-yellow needles. By electrolytic reduction in alcohol and 20% sulphuric acid at  $50-60^\circ$  and a current density 0.06 ampere per sq. cm. at the cathode, *isopropylidihydroberberine* yields the two stereoisomerides, *isopropyltetrahydroberberine*,

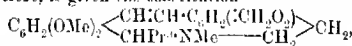


m. p.  $157-158^\circ$ , greenish-yellow, rhombic leaflets (*sulphate*, m. p.  $197^\circ$  [decomp.]; *nitrate*, decomp.  $215^\circ$ ; *hydrochloride*, decomp.  $226^\circ$ ; *platinichloride*, decomp.  $205^\circ$ ; *perchlorate*, m. p.  $226-227^\circ$  [decomp.]), and  $\psi$  *isopropyltetrahydroberberine*, m. p.  $200-202^\circ$ , colourless prisms (*nitrate*, decomp.  $176^\circ$ ; *hydrochloride*, decomp.  $254^\circ$ ). By treatment with alcoholic iodine at  $100^\circ$ , *isopropyltetrahydroberberine* is converted

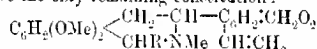
into *isopropylidihydroberberine hydriodide*,  $C_{23}H_{25}O_4N.HI.Et.OH$ , decomp.  $110^\circ$ , brown, rhombic plates, whilst the  $\psi$ -base is simply converted into its hydriodide.

*isopropyltetrahydroberberine methiodide*, m. p.  $210^\circ$  (decomp.), colourless needles, and  $\psi$ -*isopropyltetrahydroberberine methiodide*, decomp.  $247-248^\circ$ , faintly yellow needles, each yield, by treatment with silver oxide and 50% alcohol, and subsequently with boiling potassium hydroxide, a mixture of *a-de-N-methylisopropyltetrahydroberberine*,  $C_{24}H_{27}O_4N$ , m. p.  $132.5^\circ$  (*sulphate*, decomp. about  $200^\circ$ ; *hydriodide*, decomp.  $197^\circ$ , yellow needles), and *b-de-N-methylisopropyltetrahydroberberine*,  $C_{24}H_{27}O_4N$ , m. p.  $102-103^\circ$  (*hydrochloride*, decomp.  $226^\circ$ ; *hydriodide*, decomp.  $218^\circ$ ; *nitrate*, decomp.  $197^\circ$ ). The *a-de*-base is converted into the *b-de*-base by boiling alcohol, and yields  $\psi$ -*isopropyltetrahydroberberine methiodide* by digestion with aqueous alcohol and subsequent treatment with acetic acid and potassium iodide: it is unchanged by boiling nitrobenzene, by boiling dilute sulphuric acid and alcohol, or by electrolytic reduction. The *b-de*-base is comparatively stable. By prolonged boiling with glacial acetic acid and subsequent treatment of the basified and filtered solution with potassium iodide, it yields a *methiodide*, m. p.  $236^\circ$ , from which the *b-de*-base is regenerated directly.

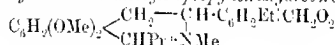
Of all the *de*-bases examined by the authors (preceding and following abstracts), *a-de-N-methylisopropyltetrahydroberberine* is the only one which resembles Gadamer and Voss's ethyl anhydro-base of tetrahydroberberine (A., 1910, i, 415) in being readily re-converted into the ammonium base or its salts by digestion with water or acids. The *a-de*-base, therefore, is given the constitution



analogous to that of the ethyl anhydro-base of tetrahydroberberine. The *b-de*-base and all other *de*-alkyl (or -aryl)-*N*-methyltetrahydroberberines have the only remaining constitution:



(compare preceding abstract). Given these constitutions, the preceding transformations of *a*- and *b-de-N-methylisopropyltetrahydroberberine* become readily explicable. By electrolytic reduction, the *b-de*-base yields *hydro-b-de-N-methylisopropyltetrahydroberberine*,



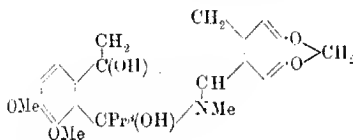
colourless needles containing alcohol, m. p.  $74-80^\circ$  (*hydrochloride*,  $C_{24}H_{27}O_4N.HCl$ , decomp.  $261^\circ$ ).

*b-de-N-methylisopropyltetrahydroberberine methiodide*,  $C_{24}H_{27}O_4N.MI$ , colourless prisms (the *a-de*-base does not form a methiodide), is converted by the usual method into *de-NN-dimethylisopropyltetrahydroberberine*,  $C_{25}H_{27}O_4N$ , m. p.  $112-115^\circ$ , colourless needles (*sulphate*, decomp. about  $129^\circ$ ). *iso*-Propylidihydroberberine and methyl iodide at  $100^\circ$  yield the *hydriodide*, decomp.  $229^\circ$ , yellow needles, of *de-N-methylisopropylidihydroberberine*,  $C_{24}H_{27}O_4N$  (for constitution, compare Freund and Fleischer, preceding abstract), m. p.  $170-171^\circ$ , pale

yellow crystals (*perchlorate*, decomp.  $213^{\circ}$ ; *methiodide*, decomp.  $232^{\circ}$ , golden-yellow, rhombic prisms).

The electrolytic reduction of *de-N-methylisopropylidihydroberberine* in alcohol and 20% sulphuric acid at  $50-60^{\circ}$  yields a mixture of  $\alpha$ -*hydro-de-N-methylisopropylidihydroberberine*,  $C_{21}H_{29}O_4N$ , m. p.  $164.5-166^{\circ}$ , greenish-yellow, rhombic plates (*nitrate*, decomp.  $185^{\circ}$ , rhombic plates; *sulphate*, m. p.  $197^{\circ}$ , prisms; *hydrochloride*, m. p. about  $218^{\circ}$ , needles; *hydriodide*, m. p.  $234^{\circ}$ ; *perchlorate*, decomp.  $236^{\circ}$ ), and  $\beta$ -*hydro-de-N-methylisopropylidihydroberberine*,  $C_{21}H_{29}O_4N$ , m. p.  $184-186^{\circ}$ , almost colourless, rhombic prisms (*nitrate*, decomp.  $188^{\circ}$ ; *hydriodide*, decomp.  $226-227^{\circ}$ ). The  $\alpha$ -compound does not form a methiodide, and yields *de-N-methylisopropylidihydroberberine* by treatment with bromine in chloroform and basification of the product. The  $\beta$ -base forms a *methiodide*,  $C_{21}H_{29}O_4NMeI$ , decomp.  $253^{\circ}$ , and is unchanged by bromine. By oxidation with sodium dichromate and

acetic acid at  $80-90^{\circ}$ , *de-N-methylisopropylidihydroberberine* and its  $\alpha$ - and  $\beta$ -hydro-derivatives each yield the same product, *hydroxyde-N-methylisopropylidihydroberberine hydroxide*



(annexed formula I), decomp.  $120^{\circ}$ , light brown crystals, which forms a *hydrochloride*, decomp. about  $205^{\circ}$ , and *hydriodide*, decomp.  $238^{\circ}$ . C. 8

**isoButylidihydroberberine and Its Derivatives.** MARTIN FREUND and HAROLD HAMMEL (*Annalen*, 1913, 397, 85-93).—*iso-Butylidihydroberberine*,  $C_{21}H_{29}O_4N$ , m. p.  $112-113^{\circ}$ , yellow needles, leaflets, or prisms, prepared in the usual manner from berberine hydrochloride and ethereal magnesium *isobutyl* bromide, forms a *nitrate*, m. p.  $205^{\circ}$  (decomp.), pale yellow leaflets, *hydriodide*, m. p.  $223^{\circ}$  (decomp.), yellow leaflets, and *platinichloride*, decomp.  $220^{\circ}$ , orange needles. It reacts with methyl iodide to form the *hydriodide*, m. p.  $206^{\circ}$  (decomp.), pale yellow needles, of *de-N-methylisobutylidihydroberberine*,  $C_{22}H_{31}O_4N$ , m. p.  $147-148^{\circ}$  (*hydrochloride*, m. p.  $148^{\circ}$  [decomp.]; *platinichloride*, m. p.  $217^{\circ}$ ; *hydrotromide*, m. p.  $115-120^{\circ}$  [decomp.]). The *de*-base is unchanged by bromine in chloroform, and forms a *methiodide*,  $C_{22}H_{31}O_4NMeI$ , m. p.  $172^{\circ}$  (decomp.), pale yellow leaflets, which is converted in the usual manner into *de-NN-dimethylisobutylidihydroberberine*,  $C_{23}H_{33}O_4N$ , m. p.  $130-131^{\circ}$ , almost colourless plates. The *methiodide* of the last substance,  $C_{23}H_{33}O_4NMeI$ , m. p.  $161^{\circ}$  (decomp.), yellow needles, decomposes into methyl iodide and the original base when heated at about  $95^{\circ}$  or boiled with aqueous alcoholic potassium hydroxide; the base is also obtained when the *methiodide* is treated successively with silver oxide and boiling potassium hydroxide.

By reduction at a lead cathode in alcohol and 25% sulphuric acid, *de-N-methylisobutylidihydroberberine* yields a mixture of  $\alpha$ -*hydro-de-N-methylisobutylidihydroberberine*,  $C_{22}H_{33}O_4N$ , m. p.  $158-160^{\circ}$ , almost

colourless, rhombic plates (*hydrobromide*, decomp.  $223^{\circ}$ ; *hydriodide*, m. p.  $189^{\circ}$ ), and  $\beta$ -*hydro-de-N-methylisobutyldihydroberberine*,  $C_{26}H_{31}O_4N$ , m. p.  $179^{\circ}$  (*hydrochloride*, decomp. about  $240^{\circ}$ ; *hydrobromide*, m. p.  $239^{\circ}$ ; *hydriodide*, m. p.  $239^{\circ}$  [decomp.]). The  $\alpha$ -compound does not form a methiodide, and is converted into *de-N-methylisobutyldihydroberberine* by treatment with bromine in chloroform and basification of the product. The  $\beta$ -compound is unchanged by bromine, and forms a *methiodide*,  $C_{26}H_{31}O_4N, MeI$ , m. p.  $246^{\circ}$  (decomp.), which regenerates the  $\beta$ -compound by heating at  $240^{\circ}$ , and is converted by successive treatment with silver oxide and boiling potassium hydroxide into  $\beta$ -*hydro-de-NN-dimethylisobutyldihydroberberine*,  $C_{26}H_{33}O_4N$ , m. p.  $136-137^{\circ}$ , colourless, rhombic leaflets. By electrolytic reduction at a lead cathode in sulphuric acid, *isobutyldihydroberberine* yields a mixture of *isobutyldihydroberberine*,  $C_{24}H_{29}O_4N$ , m. p.  $127-129^{\circ}$ , greenish-yellow, rhombic leaflets (*hydrochloride*, m. p.  $237^{\circ}$ ; *hydriodide*, m. p.  $256^{\circ}$ ; *sulphate*, m. p.  $231^{\circ}$ ; *methiodide*, m. p.  $193^{\circ}$ ), and  $\psi$ -*isobutyldihydroberberine*,  $C_{24}H_{29}O_4N$ , m. p.  $197^{\circ}$ , colourless plates (*hydrochloride*, m. p.  $270-273^{\circ}$  [decomp.]; *hydriodide*, m. p.  $250^{\circ}$  [decomp.]).  
C. S.

*n*-*Octyldihydroberberine* and *isoAmyldihydroberberine* and their Derivatives. MARTIN FREUND and DANIEL STEINBERGER (*Annalen*, 1913, 397, 94-106).—A suspension of berberine sulphate in ether, by treatment with ethereal magnesium *n*-octyl iodide and decomposition of the product by ice and hydrochloric acid, yields the *hydriodide*,  $C_{28}H_{35}O_4N, HI, H_2O$ , m. p.  $122-124^{\circ}$ , reddish-brown crystals, of *octyldihydroberberine*,  $C_{28}H_{35}O_4N$ , m. p.  $88.5-89^{\circ}$ , yellow needles. In a similar manner, berberine sulphate and magnesium *isoamyl* bromide, after the addition finally of concentrated potassium iodide, yield the *hydriodide*, decomp.  $141^{\circ}$ , yellow crystals, of *isoamylidihydroberberine*,  $C_{26}H_{31}O_4N$ , an amorphous, yellow substance.

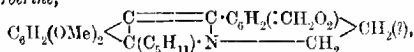
By reduction with stannous chlorido, hydrochloric acid, D 1.13, and alcohol, *isoamylidihydroberberine* yields only *isoamyltetrahydroberberine*,  $C_{26}H_{31}O_4N$ , m. p.  $95-96^{\circ}$  (*sulphate*, decomp.  $237^{\circ}$ ; *hydriodide*, decomp.  $255^{\circ}$ ; *nitrate*, decomp.  $209-210^{\circ}$ ), whilst by reduction at a lead cathode in alcohol and 20% sulphuric acid at  $40-50^{\circ}$ , it yields, in addition,  $\psi$ -*isoamyltetrahydroberberine*,  $C_{25}H_{31}O_4N$ , m. p.  $172^{\circ}$  (*hydrochloride*, decomp.  $231-232^{\circ}$ ; *hydriodide*, decomp.  $239-240^{\circ}$ ; *nitrate*, decomp.  $210-211^{\circ}$ ).

*isoAmyltetrahydroberberine methiodide*, decomp.  $191^{\circ}$ , and  $\psi$ -*isoamyltetrahydroberberine methiodide*, decomp.  $223-224^{\circ}$ , each yield, by the usual method of decomposition, *de-N-methylisoamyltetrahydroberberine*, which forms a *hydrochloride*,  $C_{26}H_{33}O_4N, HCl$ , decomp.  $185^{\circ}$ , *sulphate*, decomp.  $190-191^{\circ}$ , and *hydriodide*, decomp.  $224-225^{\circ}$ , and does not yield hydrastinine by oxidation.

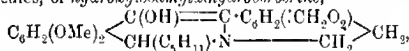
*isoAmyldihydroberberine* and methyl iodide at  $100^{\circ}$  yield the *hydriodide* of *de-N-methylisoamylidihydroberberine*,  $C_{26}H_{31}O_4N$ , m. p.  $102^{\circ}$ , pale yellow plates. By reduction with stannous chlorido, hydrochloric acid, and alcohol, the *de-base* yields  $\alpha$ -*hydro-de-N-methylisoamylidihydroberberine*,  $C_{26}H_{33}O_4N$ , m. p.  $128^{\circ}$ , rhombic leaflets, which forms a *sulphate*, decomp.  $187-188^{\circ}$ , *nitrate*, decomp.  $146^{\circ}$ , *hydro-*

*chloride*, decomp. 232°, and *hydriodide*, decomp. 228°, does not form a methiodide, and is converted into *de-N-methylisoamylidihydroberberine* by treatment with bromine in chloroform. By reduction at a lead cathode, *de-N-methylisoamylidihydroberberine* yields, in addition to the preceding  $\alpha$ -compound,  $\beta$ -*hydro-de-N-methylisoamylidihydroberberine*,  $C_{28}H_{31}O_4N$ , m. p. 145°, rhombic prisms (*hydrochloride*, decomp. 220—221°; *hydriodide*, decomp. 226—227°; *methiodide*, m. p. 260°).

By prolonged heating with alcoholic ammonia in the presence of air, *isoamylidihydroberberine* hydriodide is converted into *dehydroisoamylidihydroberberine*,



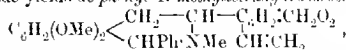
m. p. 249° (decomp.), hexagonal, yellow plates, which rapidly darken in the air and light. The dehydro-compound yields *isoamyl-* and  $\psi$ -*isoamyl-tetrahydroberberines* by electrolytic reduction, does not form salts with acids in the cold, and by boiling for eight to ten minutes with 96% alcohol and 20% hydrochloric acid or sulphuric acid, D 1.215, is converted into the *hydrochloride*,  $C_{25}H_{29}O_3N \cdot HCl$ , decomp. 204°, yellow needles, or the *sulphate*,  $C_{25}H_{29}O_3N \cdot H_2SO_4$ , decomp. 265°, yellow needles, of *hydroxyisoamylidihydroberberine*,



m. p. 120—125°, sintering at 65°, dark yellow needles; a by-product of both reactions is a *substance*, decomp. 180—185°, reddish-brown, rhombic crystals. C. S.

**Phenylidihydroberberine and its Derivatives.** MARTIN FREUND and EUGEN ZORN (*Annalen*, 1913, 397, 107—117).—Phenylidihydroberberine (Freund and Beck, A., 1903, i, 151) forms a *hydrochloride*, m. p. 160°, yellow prisms, *sulphate*, decomp. 170°; pale yellow needles, *nitrate*, decomp. 221°, and *hydriodide*, m. p. 215°. By reduction at a lead cathode in alcohol and 30% sulphuric acid, it yields Gadamer's phenyltetrahydroberberine (*sulphate*, decomp. 241°), and  $\psi$ -phenyltetrahydroberberine,  $C_{25}H_{27}O_3N$ , m. p. 204—205°, white needles (*hydriodide*, m. p. 235°); only the former can be isolated when the reduction is effected by stannous chloride and boiling alcohol and hydrochloric acid.

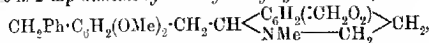
*Phenyltetrahydroberberine methiodide*, m. p. 243°, faintly yellow plates, and  $\psi$ -phenyltetrahydroberberine *methiodide*, m. p. 247°, white crystals, yield methyl iodide and the respective bases by heating. By treatment with silver oxide and boiling potassium hydroxide in the usual manner, each methiodide yields *de-phenyl-N-methyltetrahydroberberine*,



m. p. 153°, which forms a *hydrochloride*, m. p. 232°, *hydriodide*, decomp. 268°, and *methiodide*, m. p. 238° (decomp.). By reduction at a lead cathode, the de-base is converted into *hydro-de-phenyl-N-methyltetrahydroberberine*,  $C_6H_5(OMe)_2 \left\langle \begin{array}{c} CH_2 - CH - \\ CHPh \cdot NMe \end{array} \right\rangle C_6H_5(C_6H_5O_2)$ , m. p. 142—143° (*hydrochloride*, m. p. 271—272°; *hydriodide*, m. p. 257°).

Phenyltetrahydroberberine methiodide is converted into the metho-

chloride in dilute alcohol, and the latter, after evaporation of the alcohol, is treated with 5% sodium amalgam on the water-bath. The product is 2-*mp-dimethoxy o-benzylbenzylhydrastinine*,



m. p. 109.5—110.5°, colourless plates (*hydriodide*, m. p. 217—219°), from which hydrastinine is obtained by oxidation with sodium dichromate and acetic acid at 90°.

Phenyldihydroberberine and methyl iodide at 100° yield the *hydr. iodide*, m. p. 245°, yellow prisms, of *de-phenyl-N-methyldihydroberberine*,  $\text{C}_{27}\text{H}_{26}\text{O}_4\text{N}$ , m. p. 178—179°, yellow prisms (*sulphate*, m. p. 160°; *methiodide*, decomp. 220°). By reduction at a lead cathode in cold alcohol and 30% sulphuric acid, the de-base is converted into a mixture of *α-hydro-de-phenyl-N-methyldihydroberberine*,  $\text{C}_{27}\text{H}_{27}\text{O}_4\text{N}$ , m. p. 178—179°, yellow, rhombic prisms (*sulphate*, m. p. 206°, colourless prisms; no *methiodide*), and *β-hydro-de-phenyl-N-methyldihydroberberine*,  $\text{C}_{27}\text{H}_{27}\text{O}_4\text{N}$ , m. p. 211—212°, rhombic plates (*hydrochloride*, m. p. 237°; *methiodide*, m. p. 247—248°, pale yellow leaflets). C. S.

**Preparation of Morphine Esters of Halogenated Fatty Acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 256156. Compare this vol., i, 385).—*Dichloroacetylmorphine*, a yellow powder, decomp. 204°, is obtained when cooled anhydrous morphine (5 parts) is slowly treated with chloroacetyl chloride (10 parts) and subsequently heated at 90—100°.

*Chloroacetylmorphine*, colourless crystals, decomp. 227°, is obtained by the partial hydrolysis of the preceding compound or by employing 6 parts of chloroacetyl chloride in the foregoing preparation. *Di-α-bromoisovalerylmorphine*, sintering at 61° and decomposing at 133°, is formed by the action of α-bromoisovaleryl chloride on morphine in the presence of pyridine. F. M. G. M.

**The Symmetry of Sparteine.** LOUIS CORRIEZ (*Chem. Zentr.*, 1913, i, 29; from *Bull. Sci. Pharmacol.*, 1912, 19, 602—610. Compare Moureu and Valeur, A., 1912, i, 296).—An attempt to prove the symmetry of the sparteine molecule was made by decomposing the hydrochloride of α-sparteine methochloride and the hydrobromide of α-sparteine methobromide in a vacuum at 250°, but the reaction was of a complicated nature, since the resulting sparteine haloids partly decomposed into sparteine. An attempt to obtain the same iodobromide by treating sparteine iodide with hydrogen bromide and sparteine bromide with hydrogen iodide was also without success. A homogeneous, faintly yellow *iodobromide*,  $\text{C}_{41}\text{H}_{58}\text{N}_2\cdot\text{HI}\cdot\text{HBr}\cdot\text{H}_2\text{O}$ , was obtained in the former case, in cubes with  $[\alpha]_D^{20} - 16.21'$ , but the latter process led to a mixture, containing, in all probability, the dibromide, diiodide, and iodobromide. J. C. W.

**Hæmopyrrole.** OSKAR PILOTY and JOSEF STOCK (*Ber.*, 1913, 46, 1008—1013. Compare A., 1912, i, 923).—Crude hæmopyrrole has been separated into two fractions, the one, hæmopyrrole-I, consisting of a mixture of bases which give crystalline salts with picric acid in ethereal solution; the other, hæmopyrrole-II, comprising bases which

either do not form a picrate or of which the picrates are soluble in ether. The hæmopyrrole-II fraction comprises only 12–13% of the whole; it consists as to more than one-half of pyrroles with less than eight atoms of carbon, the remainder containing pyrroles with eight carbon atoms. It consists of at least three components differing from the five hæmopyrroles already known, and the lowest boiling fraction forms a very soluble, orange-coloured picrate, m. p. 108°, whilst a high boiling fraction closely resembles bisdimethylpyrrole (Piloty and Wilke, A., 1912, i, 899). E. F. A.

**Preparation of a Dichloroisatin [and of 5:7-Dichloroisatin].** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255772 and 255774. Compare A., 1909, i, 966).—When an aqueous solution or suspension of isatin, or of 5-chloroisatin (m. p. 247°), is chlorinated at the ordinary temperature in the presence of potassium iodide, it gives rise to an unstable *dichloroisatin*, which crystallises from acetic acid in hard, red crystals, and has m. p. 155°; when this is dissolved in sodium hydrogen sulphite it loses chlorine, and the subsequent addition of acid precipitates 5-chloroisatin, whilst by the action of concentrated sulphuric acid at 80° in the presence of iodine the labile chlorine atom migrates into the ring, yielding 5:7-dichloroisatin (m. p. 221°). F. M. G. M.

**Preparation of a Dichlorobromoisatin.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255773 and 255775. Compare preceding abstract).—When an aqueous suspension of 5-bromoisatin is treated at about 15° with chlorine in the presence of potassium iodide, it furnishes a *chloro-5-bromoisatin* (red prisms, m. p. 145°), in which the chlorine atom is labile and eliminated by the action of sodium hydrogen sulphite, whilst with concentrated sulphuric acid at 80° in the presence of potassium iodide it yields 7-chloro-5-bromoisatin, yellow needles, m. p. 231°. F. M. G. M.

**Lepidylamine.** PAUL RABE (*Ber.*, 1913, 46, 1024–1025).—4-Cyanoquinoline is reduced, either on treatment with nascent hydrogen or on shaking with molecular hydrogen and a palladium sol, to 1-aminomethylquinoline (*lepidylamine*),  $C_8H_4 \begin{smallmatrix} < C(CH_2 \cdot NH_2) \\ \backslash \\ N = \\ / \\ CH \end{smallmatrix}$ . This is a colourless oil, b. p. 172°/8 mm., but becomes violet on exposure to the air. The *monohydrochloride*, which is neutral to litmus, forms a colourless, crystalline powder, m. p. 206–208° (decomp.), which becomes blue on exposure to air. The *dihydrochloride* crystallises in well formed, colourless needles, decomp. above 250°. It is acid to litmus. E. F. A.

**Quinoyl Ketones. I.** PAUL RABE and RICHARD PASTERNAK (*Ber.*, 1913, 46, 1026–1032).—By the interaction of magnesium phenyl bromide and ethyl cinchonate under special conditions, phenyl 4-quinoyl ketone, m. p. 60°, is obtained. This differs from the compound, m. p. 294°, described under the same name by Remfry and Decker (A., 1908, i, 364). In addition to ketones the esters of quinoline-4-



carboxylic acid give rise to carbinols when submitted to the Grignard synthesis. Similarly, 4-cyanoquinolines give rise to ketones and amines; thus 4-cyanoquinoline and magnesium ethyl iodide yield 4-quinolyl ethyl ketone and 4-quinolyldiethylaminomethane. In addition some quantity of 4-ethylquinoline is formed.

4-Benzylquinoline is a viscid, strongly refractive, yellow oil, b. p. 222—223°/19 mm.; the *sulphate* forms colourless, rhombic crystals + 2H<sub>2</sub>O, m. p. 105—108°, or anhydrous, m. p. 132—133°. The *picrate* forms yellow prisms and plates, m. p. 178°; the *methiodide* crystallises in orange plates, m. p. 226°.

Phenyl 4-quinolyl ketone, m. p. 60°, yields the following salts: the *picrate*, crystallising in pale yellow, interlaced needles, m. p. 220°; a *picrolonate*, forming dark yellow, rhombic crystals, decomp. 174°; an orange *methiodide*, with metallic lustre, m. p. 218°; an *oximehydrochloride*, separating in matted needles, m. p. 256° (decomp.).

4-Quinolylethylketone is a yellow oil, b. p. 163—166°/8—9 mm.; the *acetate* forms colourless needles, m. p. 87°. The *oximino*-derivative crystallises in short, colourless crystals, decomp. about 220°.

4-Quinolyl-diethylcarbinol crystallises in lustrous, colourless plates, m. p. 135°, b. p. 192—198°/13 mm.

4-Quinolyl-diethylaminomethane crystallises in colourless plates, m. p. 126°. E. F. A.

**Quinolyl Ketones. II.** PAUL RABE and RICHARD PASTERNAK (*Ber.*, 1913, 46, 1032—1034).—Ethylquinolinecarboxylates in presence of sodium ethoxide condense with esters of the general constitution R<sub>1</sub>·CH<sub>2</sub>·CO<sub>2</sub>R<sub>2</sub>; thus ethylcinchonate and ethylacetate combine to form ethyl-γ-quinoloylacetate,  $\begin{matrix} \text{N} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{CH} \cdot \text{CH} \end{matrix} \gg \text{C} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2$ , a yellow oil,

which could not be distilled unchanged, and is characterised by forming a sparingly soluble acid sulphate. When heated with 25% sulphuric acid, 4-quinolyl methyl ketone is obtained.

Similarly, ethyl quinate and ethyl propionate condense to form ethyl β-[6-methoxy-4-quinoloyl]-propionate. This is characterised by the *picrate* crystallising in slender, yellow needles, m. p. 137—138°, and the *picrolonate*, orange, matted needles, decomp. 136°.

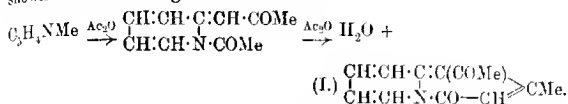
β-6-Methoxyquinolyl ethyl ketone, obtained on hydrolysis, crystallises in pale yellow needles, m. p. 57—58°. E. F. A.

**Nature of Picolide and Pyrindole.** Action of Propionic Acid on α-Picoline. MAX SCHOLTZ and W. FRAUDE (*Ber.*, 1913, 46, 1069—1082. Compare A., 1912, i, 385, 648).—Derivatives of pyrrocoline have previously been prepared by Angeli (A., 1890, 1156), who termed the compound pyrindole, and this name is now adopted by the authors.

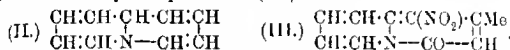
From the absence of basic properties and the formation of condensation products with only one molecule of phenylhydrazine, hydroxylamine, and semicarbazide, the conclusion is drawn that picolide contains one of its carbonyl groups directly attached to the nitrogen atom. This view is confirmed by the fact that towards alkyl

magnesium haloids, picolide behaves as a monoketone; it reacts with only one molecule of the organo-magnesium compound, yielding tertiary alcohols of the formula  $C_{10}H_8ON \cdot CMe \cdot OH$ .

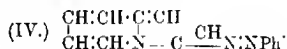
The reactions of picolide and its transformation into pyrindole are best represented by the formula I, its formation from  $\alpha$ -picoline being shown in the following scheme:



On account of its relationship to quinoline, the parent ring system (II) is termed quinolizine. Picolide is thus acetylmethylketoquinolizine, whilst the mono-nitro-compound obtained by the action of nitric acid is nitromethylketoquinolizine (III):

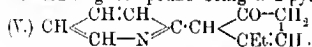


Pyrindole couples with diazonium salts in acid solution, yielding crystalline azo-compounds, and reacts with acetic anhydride and benzoyl chloride to form an acetyl and benzoyl derivative. The position of the azo- and acyl-groups has not been definitely established, but from the analogous reactions with pyrrole it is assumed that the groups enter the  $\alpha$ -position to the pyrrole ring; benzene-azopyrindole thus receives the formula:



A number of other reactions, illustrating the similarity in the behaviour of pyrindole on the one hand and pyrrole and indole derivatives on the other, are also described.

The ready formation of picolide from  $\alpha$ -picoline and acetic anhydride has induced the authors to investigate the behaviour of  $\alpha$ -picoline towards other anhydrides, but only in the case of propionic anhydride could a definite product be isolated. The reaction proceeds in a manner entirely different to that occurring when acetic anhydride is employed, the resulting compound being a 2-pyridyl-3-ethyl- $\Delta^3$ -cyclopentenone:

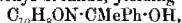


The following condensation products were obtained by condensing aromatic aldehydes with picolide by means of sodium hydroxide in alcoholic solution:

*Di-o-nitrobenzylidenepicolide*, yellowish-brown crystals, which begin to decompose at  $200^\circ$ , m. p.  $220^\circ$ ; the isomeric *meta*- and *para*-compounds have m. p.  $212^\circ$  and  $316^\circ$  respectively; *mono-p-nitrobenzylidenepicolide*, orange needles, m. p.  $242^\circ$ ; *tetramethyldi-p-aminobenzylidenepicolide*, from *p*-dimethylaminobenzaldehyde, forms orange needles, m. p.  $227^\circ$ ; *dianisylidenepicolide*, m. p.  $212^\circ$ .

Picolide reacts with magnesium methyl iodide to form the compound,  $C_{10}H_8NO \cdot CMe_2 \cdot OH$ , crystallising in long, yellow needles, m. p.  $169^\circ$ ,

and with magnesium phenyl bromide, yielding the compound,



which forms colourless, felted needles, m. p. 178°.

*Benzeneazopyrindole* (formula IV) crystallises in red needles, m. p. 109°, and *pyrindoleazo-p-toluene* in reddish-brown needles, m. p. 98°.

*α-Naphthaleneazopyrindole* forms a brown, crystalline powder, which begins to melt at 120° and then decomposes.

*Benzoylpyrindole*,  $\text{C}_8\text{H}_6\text{N} \cdot \text{COPh}$ , prepared by the interaction of pyrindole and benzoyl chloride at the ordinary temperature, crystallises in yellow needles, m. p. 96°.

Pyrindole reacts with carbonyl chloride in toluene solution to form *pyrindolecarboxyl chloride*,  $\text{C}_8\text{H}_6\text{N} \cdot \text{COCl}$ , which crystallises in colourless needles, m. p. 81°, and is hydrolysed by aqueous sodium hydroxide to *pyrindolecarboxylic acid*, needles, m. p. 135° (decomp.).

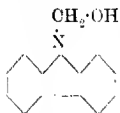
*Diquinonylpyrindole*,  $\text{CH}:\text{CH}:\text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_4\text{O}_2$ , prepared from pyrindole and quinone in alcoholic solution, forms deep blue crystals, m. p. above 350°, and resembles the diquinonyldimethylpyrrole described by Mühlau and Redlich (A., 1912, i, 129°).

Pyrindole condenses with ethyl acetoacetate in alcoholic solution in the presence of hydrochloric acid, yielding *ethyl dipyrindoleacetoacetate*,  $\text{CH}:\text{CH}:\text{C} \equiv \text{C} \cdot \text{CMe}(\text{CH}_2\text{CO}_2\text{Et}) \cdot \text{C} \equiv \text{C} \cdot \text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{N} \cdot \text{CH}:\text{CMe}(\text{CH}_2\text{CO}_2\text{Et}) \cdot \text{C} \cdot \text{CH}:\text{N} \cdot \text{CH}:\text{CH}$ , crystallising in microscopic, yellowish-green needles, m. p. 140°.

*2-Pyridyl-3-ethyl-Δ²-cyclopentenone* (V), prepared by heating *α*-picoline and propionic anhydride at 220°, forms colourless needles, m. p. 86°, and yields a *semicarbazone*, yellow needles, m. p. 201°. F. B.

#### Preparation of Methylolcarbazole. MARTIN LANGE (D.R.P.

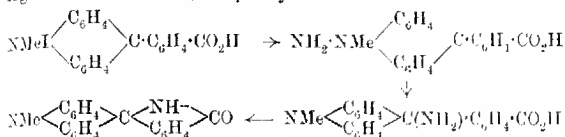
256757).—*Methylolcarbazole* (annexed formula) is obtained when a boiling alcoholic solution of carbazole (16.7 parts) is treated with anhydrous potassium carbonate (10 parts) and a 40% solution of formaldehyde (10 parts); on cooling, the product separates; it forms colourless needles, m. p. 127–128°, with an evolution of formaldehyde. mineral acids convert it into methylenecarbazole. F. M. G. M.



**Preparation of *N*-Alkylcarbazolesulphonic Acids.** LEONOLD CASSELLA & Co. (D.R.P. 256718. Compare A., 1910, i, 775).—Sulphonated *N*-alkylcarbazoles have not been prepared, although di- and tri-sulphonyl derivatives of carbazole itself are known. *Ethyl carbazolesulphonic acid* is obtained when fused *N*-ethylcarbazole (195 parts) is slowly treated with forty parts of concentrated sulphuric acid, heated at 120° and subsequently at 150–160°, and the mixture finally treated with sodium carbonate; the barium, calcium, sodium, and potassium salts are crystalline powders.

When fused with an alkali hydroxide, these compounds furnish hydroxy-*N*-alkylcarbazoles, which condense with *p*-nitrosophenols to yield indophenolsulphonic acids. F. M. G. M.

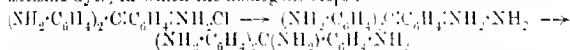
**Ammonium amides and the Action of Amines on Cyclammonium Salts and Analogous Compounds.** HERMAN DECKER and PAUL BECKER (*Ber.*, 1913, 46, 969—978).—It has already been shown that the action of ammonia or amines on the quaternary salts of phenylacridinecarboxylic acid yields not only the lactone, but also the lactam of aminophenylmethyl-dihydroacridinecarboxylic acid (Decker and Schenk, A., 1906, i, 304), and it was suggested that the change takes place with the intermediate formation of a compound corresponding to ammonium-amide,  $\text{NH}_4 \cdot \text{NH}_2$ , the scheme:



representing the probable series of changes. This view was confirmed by several considerations, and it is now greatly strengthened by the discovery that the parent substance, phenylacridine methiodide, is converted by concentrated ammonia into 5-amino-5-phenyl-10-methyl-dihydroacridine,  $\text{NMe} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CPh} \cdot \text{NH}_2$ . This finally disposes of any idea that the previous product may have been due to the action of ammonia on the previously formed lactone. The cause of the rearrangement is supposed to be the tendency of the positive amino-group to migrate from the positive nitrogen atom to a negative

carbon atom. That such a substance as  $\text{NH}_2 \cdot \text{NMe} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CPh}$ ,

which is assumed as the first product of the above reaction, should be capable of at least a fleeting existence is indicated by the formation of carbonylamines by the action of ammonia on the salts of the triphenyl-methane dyes, in which the analogous steps:



probably occur (Noelting and Saas, this vol. i. 522; Villiger and Kopperschmid, A., 1912, i, 1030). The structurally related xanthylium and thioxanthylium salts also yield carbonylamines with ammonia. The possibility that the acridinium salts may be of the carbonylamine structure which has been suggested for the triphenylmethane colours is very slight, as the former eliminate methyl iodide exceedingly readily, even, for example, when exposed in aqueous solution to daylight for several weeks.

5-Amino-5-phenyl-10-methyl-dihydroacridine, small, colourless rods, m.p. 121—122°, is obtained by the gradual addition of a concentrated solution of phenylacridine methiodide to a large excess of 20% ammonia solution; if a dilute solution of ammonia in slight excess is allowed to act on the methiodide, the product is hydroxyphenylmethyl-dihydroacridine, which is very similar in appearance, and this accounts for the divergence of the results of Decker, Hock, and Djiwonsky (A., 1902,

i, 830) and of Hantzsch (A., 1902, i, 113, 126). The above amino-compound dissolves in dilute acids, undergoing scission into phenyl-methylacridinium and ammonium salts; when heated with alcohol, with or without the addition of a little sodium hydroxide, ammonia is again obtained, together with the 5-ethoxy-5-phenyl-10-methyldihydro-acridine, colourless prisms, m. p. 112–113°, which is also obtained by similar treatment of the hydroxyphenylmethyldihydroacridine itself. When warmed with aniline, both the above amino-compound (a carbonylamine) and the corresponding hydroxy-compound are converted into the *carbonylanilide* with elimination of a molecule of ammonia and of water respectively.

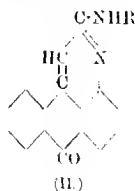
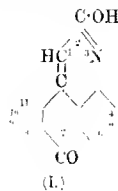
If a solution of a phenylxanthylum salt is introduced into ammonia solution a mixture of the amino-compound and of the carbonyl is obtained (compare Bünzly and Decker, A., 1904, i, 912); for the preparation of the pure amino-compound the phenylxanthylum ferrichloride, m. p. 169°, was introduced as a fine powder into 20% ammonia solution under benzene; the resultant carbonylamine (9-amino-9-phenyl-xanthen),  $O \left\langle \begin{smallmatrix} C_6H_5 \\ C_6H_5 \end{smallmatrix} \right\rangle CPh \cdot NH_2$ , leaflets, m. p. 112–113°, is extracted by the benzene; when boiled with alcohol it is converted into the ethyl ether of phenylxanthenol (Bünzly and Decker, *loc. cit.*). The formation of the carbonylamine is believed to follow the same course as with the corresponding acridino compound.

9-Amino-9-phenylthioxanthen, yellowish-red prisms, m. p. 118–120°, is obtained in a similar manner by the action of ammonia on phenylthioxanthylum ferrichloride, and undergoes similar conversion into the ethyl ether of thioxanthenol.

The recent discovery of Zincke and Weisspfennig (this vol., i, 389) of dinitrodiphenylamine amongst the reaction products of aniline and 2-dinitrophenylisquinolinium chloride is held to be a further confirmation of the existence of the ammonium-anilides and of their decomposition according to the equation:  $NA_1 \cdot NR_2 = NA_2 + NR_2A$ , where A represents an alkyl radicle.

D. F. T.

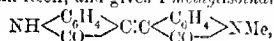
**Preparation of Anthracene Derivatives Containing Nitrogen**  
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 256257. Compare A., 1908, i, 456, 699; 1909, i, 263).—*α-Chloropyridanthrone*, yellowish-white needles, m. p. 260°, is prepared by the action of phosphorus pentachloride on the previously described 2-hydroxypyridanthrone (I); it reacts readily with primary aromatic amines to furnish compounds of the general formula (II).



2(1')-*Anthraquinonylaminopyridanthrone* is thus obtained by condensation with 1-aminoanthraquinone in nitrobenzene solution in the presence of copper iodide and sodium acetate; it does not melt below 300°. The analogous compound from anilino has m. p. 227–229°.

F. M. G. M.

**Syntheses in the Group of the Indogenides.** ANDRÉ WAHL and P. BAGARD (*Compt. rend.*, 1913, 156, 898–901).—An endeavour to prepare, by the condensation of substituted isatins with oxindole, a new series of indogenides of the type  $X \begin{smallmatrix} \text{C}_6\text{H}_3\text{R} \\ \text{CO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{C}_6\text{H}_3\text{R}' \\ \text{CO} \end{smallmatrix} \text{Y}$ , where X and Y may be identical or different bivalent atoms or groups, and R and R' any substituents. These condensations did not, however, go so simply as in the case of isatin itself and oxindole (compare A., 1909, i, 330). Thioisatin and oxindole yields not thio-3:3'-bisindole, as expected, but "thioindigo scarlet,"  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$  (compare Kalle, D.R.-P. 241327). 1-Methylisatin on the other hand behaves like isatin itself, and gives 1-methylthioindigotin,



brown needles.

2-Methylisatin when mixed with oxindole in acetic acid solution containing a little aqueous hydrochloric acid is hydrolysed and the product of condensation is simply 3:3'-bisindole. If the action takes place in an anhydrous medium in the cold, indirubin is formed. This thus furnishes an easy and rapid method of preparing indirubin, and gives a 90% yield.

W. G.

[Preparation of 1-Chloronitro-2:4-diacetylphenylenediamine.] AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 255858).—1-Chloro-2:4-phenylenediamine gives rise to a diacetyl derivative which on nitration furnishes 1-chloronitro-2:4-diacetylphenylenediamine, m. p. 234–235°, and on hydrolysis yields 1-chloronitro-2:4-phenylenediamine, m. p. 170°.

F. M. G. M.

**Existence of Phenyl-di-imide.** WILHELM VACHEL (*Ber.*, 1913, 46, 1115–1116. Compare A., 1900, i, 522).—An acknowledgment of the criticism of Forster and Withers (T., 1913, 103, 266) as to the nature of the compound described as phenyl-di-imide.

H. W.

[Preparation of Anthraquinone Derivatives.] FARBWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.-P. 256626).—3-Bromo-4-aminoanthraquinoneacritone, a blue powder, m. p. 260–270°, is obtained when 3-bromo-4-amino-1-anthraquinenylnthranilic acid is heated at 30° with chlorosulphonic acid.

F. M. G. M.

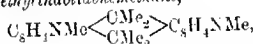
[Preparation of Indigoid Compounds.] BADISCHE ANILIN- & SONA-FABRIK (D.R.-P. 255691. Compare A., 1906, i, 696).—The compound,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{X}$ , dark red needles, m. p. 212°

(decomp.), is obtained by the action of alkali hydroxides on indoxyl; if the action is allowed to proceed further, it gives rise to the *comp.*  
 pound,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO}_2\text{H} \end{smallmatrix} \text{CH} : \text{C} \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{N}$ , and this, when boiled with an alkali carbonate, furnishes anthranilic acid and  $\beta$ -indolealdehyde (*loc. cit.*).  
 F. M. G. M.

**Action of Aliphatic Ketones on Indole and its Homologues: Polymeric Indoles.** MAX SCHOLTZ (*Ber.*, 1913, 46, 1082—1089).—Indole and its 2-methyl derivative condense with acetone, yielding compounds of the type: (I)  $\text{N} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{CMe}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{N}$  and

(II)  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{CMe}_2 \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{NH}$ , accordingly as the condensation is effected by means of hydrochloric acid or acetic acid. Similar products are obtained from methyl ethyl ketone, but not from diethyl ketone.

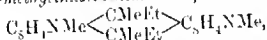
*Bisdimethyl-2-methylindolidenemethane,*



obtained in the form of its *hydrochloride* (colourless needles, m. p. 172°) by the addition of hydrochloric acid to an alcoholic solution of 2-methylindole and acetone, crystallises in colourless needles, m. p. 183°; the *hydrobromide*, prepared in a similar manner, has m. p. 172°.

*Bis-2-methylindylidimethylmethane*,  $\text{CMe}_2(C_8H_7NMe)_2$ , is obtained by boiling 2-methylindole with glacial acetic acid; it crystallises in colourless leaflets, m. p. 197°.

*Bismethylethyl-2-methylindolidenemethane,*



prepared from methyl ethyl ketone, using hydrochloric acid as the condensing agent, forms colourless leaflets, m. p. 97°; the *hydrochloride* crystallises in colourless needles, m. p. 166°.

Ethyl acetoacetate and 2-methylindole yield *ethyl 2-methylindolidenacetate*,  $\text{N} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CMe} \end{smallmatrix} \text{C} \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , crystallising in long, colourless needles, m. p. 124°.

*Bisdimethylindolidenemethane* (formula I), prepared from indole and acetone, forms light yellow needles, m. p. 170°; the *hydrochloride* crystallises in orange-yellow needles, m. p. 169°.

*Bis-2-ethylindylidimethylmethane* (II) forms colourless prisms, m. p. 165°.

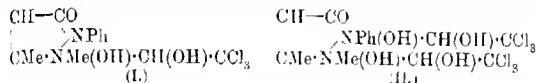
An alcoholic solution of indole, on treatment with hydrochloric acid at the ordinary temperature, yields the *hydrochloride* of tri-indole, crystallising in prisms, m. p. 183°; replacement of the hydrochloric acid by hydrobromic acid gives rise to the *hydrobromide* of di-indole, which forms slender, colourless needles (compare Keller, this vol. i. 403).  
 F. B.

**The Constitution of the Pyrazolinecarboxylic Acids. III.** AUGUST DARAPSKY (*Ber.*, 1913, 46, 863—867).—An experimental

investigation in favour of the view that the condensation products of the esters of the diazo-aliphatic acids with the esters of unsaturated carboxylic acids are in reality pyrazolino derivatives and not azine compounds with open-chain structure (compare Darapsky, this vol., i, 297; A., 1912, i, 391; Bülow, this vol., i, 101; A., 1912, i, 134, 316).

The reduction of 4-phenylpyrazole-3:5-dicarboxylic acid by sodium amalgam and water at 80–90° gave the same 4-phenylpyrazolidine-3:5-dicarboxylic acid (Buchner and Perkel, A., 1904, i, 101) as was obtained by a similar reduction of 4-phenylpyrazolino-3:5-dicarboxylic acid. The temperature of decomposition of the product ranges between 220° and 226° according to the rate of heating. D. F. T.

**Constitution of Hypnal.** DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1913, [iv], 13, 281–285).—Béhal and Choay (A., 1893, i, 301) have obtained two substances by the action of chloral on antipyrine, to which they assign the formulæ below, the first of which is used in



pharmacy under the name hypnal. For the second, the author proposes the name bihypnal. The substances have m. p. 62.3° and 61.8° respectively, whereas Béhal and Choay found 67–68° for either substance.

The author has examined the freezing-point curve of mixtures of chloral hydrate and antipyrine, and finds that it rises to a maximum at the two points at which chloral hydrate: antipyrine = 2:1 and 1:1 respectively. From the general form of the curve, he is led to the conclusion that hypnal and bihypnal are molecular compounds, which, he considers, explains the practical identity of their m. p.'s

H. W.

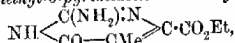
**Some New Derivatives of Piperazine.** MARIO CHICLIENO (*Atti R. Accad. Sci. Torino*, 1912–13, 48, 534–538).—When cyan-acetic ester and anhydrous piperazine are heated together for one hour at 100–115°, *biscyanoacetyl piperazine*,  $\text{C}_4\text{H}_8\text{N}_6(\text{CO} \cdot \text{CH}_2 \cdot \text{CN})_2$ , is formed; it crystallises in colourless or slightly yellow needles, m. p. 248–250° (decomp.). When ordinary hydrated piperazine is used in the reaction, the corresponding *amide*,  $\text{C}_4\text{H}_8\text{N}_6(\text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$ , is obtained; it crystallises in colourless needles or in prisms, which decompose about 174–175° when rapidly heated. The substance is acid in reaction, and gives metallic salts. It is converted into the dicarboxylic acid only with great difficulty. Anhydrous piperazine, m. p. 104°, is obtained by keeping ordinary piperazine over calcium chloride for a long time. R. V. S.

**Pyrimidines. LX. Alkylation with Benzyl Chloride.** TREAT B. JOHNSON and ZAI ZIANG ZEE (*Amer. Chem. J.*, 1913, 49, 287–294).—Johnson and Derby (A., 1908, i, 1018) studied the action of benzyl chloride in presence of sodium ethoxide on certain derivatives



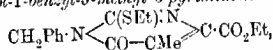
of 2-ethylthiol-6-pyrimidone, and found that in all cases the corresponding *N*-benzyl compounds were produced. It was shown that the substitution of a methyl group in the 4- or 5-position and a bromine atom or ethoxy-group in the 5-position of the ring does not favour the formation of 6-benzoxypyrimidines. The present work was undertaken with the object of investigating the action of benzyl chloride on a 2-thiol-6-pyrimidone in which both the 4- and 5-positions are substituted, and of determining whether a strongly negative group in the 4-position would favour the production of an *O*-benzyl derivative.

*Ethyl 2-amino-5-methyl-6-pyrimidone-4-carboxylate*,



obtained in small yield by the action of the sodium salt of ethyl oxalylpropionate on guanidine thiocyanate in presence of sodium hydroxide, forms prismatic needles, and does not show a definite m. p.

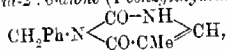
*Ethyl 2-ethylthiol-1-benzyl-5-methyl-6-pyrimidone-4-carboxylate*,



m. p. 69—71°, prepared by heating ethyl 2-ethylthiol-5-methyl-pyrimidone-5-carboxylate with benzyl chloride in presence of sodium ethoxide, crystallises in colourless needles, and when hydrolysed with concentrated hydrochloric acid is converted into 1-benzyl-5-methyl-

pyrimid-2:6-dione-4-carboxylic acid,  $\text{CH}_2\text{Ph}\cdot\text{N} \begin{array}{c} \text{CO}-\text{NH} \\ \diagup \quad \diagdown \\ \text{CO}-\text{CMe} \end{array} \text{C}\cdot\text{CO}_2\text{H}$ ,

m. p. 277—279° (decomp.), which forms hexagonal tablets. When the latter compound is heated at 285—295° until effervescence ceases, 1-benzyl-5-methylpyrimid-2:6-dione (1-benzylthymine),



m. p. 203—205°, is obtained, which forms prismatic crystals.

An attempt was made to alkylate ethyl 5-methylpyrimid-2:6-dione-4-carboxylate with benzyl chloride in presence of sodium ethoxide, but without success.

E. G.

[Phenazine] Correction. FRIEDRICH KEHRMANN (*Ber.*, 1913, 46, 1220. Compare this vol. i, 298).—Fischer and Hepp (*A.*, 1897, i, 257) had already observed that rosindones resulted by the action of alkalis on alkylmaphthaphenazonium salts. The author still holds that the green methylphenazonium iodide is a quinhydrone salt (compare Hantzsch, this vol. i, 393.)

J. C. W.

The Triphenylmethane Colour Bases. EMILIO NOELTING and J. SAAS (*Ber.*, 1913, 46, 952—967).—The authors have convinced themselves that the action of ammonia on triphenylmethane dyes is, as was believed by von Baeyer (*A.*, 1910, i, 249), more complex than was at first supposed (Noelting & Philipp, *A.*, 1908, i, 295). An independent investigation of the products of the action of ammonia has been recently published by Villiger and Kopetschni (*A.*, 1912, i, 1030).

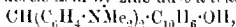
Commercial crystal-violet always contains some of the pentamethyl compound, which can be detected by acetylation, dissolving in water, and partly immersing in the liquid a piece of filter paper; the green colour of the acetyl derivative of the pentamethyl compound rises in the paper more rapidly than the violet. Even when Michler's ketone is condensed with pure dimethylaniline in the presence of phosphoryl chloride, the condensation product contains a quantity of pentamethyl compound. The product contains least pentamethyl compound if a large excess of the amine is taken for the condensation. The colourless substance obtained from the action of ammonia on crystal-violet is the carbinylamine,  $\text{NH}_2 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ ; it separates from a mixture of benzene and ligroin in prismatic tablets, m. p. 193–195°. The action of diethylamine on a solution of crystal-violet, on the other hand, precipitates the carbinol, m. p. 194–195°, which after recrystallisation has m. p. 207–209° (compare Villiger and Kopetschni, *loc. cit.*), whilst trimethylamine solution produces at first a violet solution of the ammonium base,  $\text{OH} \cdot \text{NMe}_3 \cdot \text{C}_6\text{H}_4(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , which shortly begins to lose its colour and to deposit the carbinol in a pure state.

Ethyl-violet (hexaethyltriaminotriphenylcarbinol), obtained from tetraethylaminoobenzophenone, diethylaniline and phosphoryl chloride alone, or mixed with benzene at 100°, on precipitation with potassium hydroxide yielded the free colourless carbinol,  $\text{OH} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_3$ , m. p. 136–137°. When recrystallised from alcohol, the carbinol undergoes partial etherification, and the *ethyl ether*,  $\text{OEt} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_3$ , m. p. 127–128°, can be readily obtained by the action of sodium ethoxide. The *carbinylamine*,  $\text{NH}_2 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_3$ , of ethyl-violet forms colourless needles, m. p. 141.5–142.5°.

Victoria-Blue B, obtained by purification of the commercial article and by condensation of pure Michler's ketone with phenyl- $\alpha$ -naphthylamine, forms deep blue tablets, m. p. 217–219°. No corresponding carbinol, carbinyl ether and amine were isolable, as the action of alkalis yielded only an *imine base*,  $\text{NPh} \cdot \text{C}_{10}\text{H}_7 \cdot \text{N}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , deep violet, prismatic tablets, which is hydrolysed by dilute sulphuric acid to Michler's ketone and phenyl- $\alpha$ -naphthylamine (compare Nathanson and Müller, A., 1889, 1188).

Night-Blue, m. p. 219–220°, yields an analogous *imine base*,  
 $\text{C}_6\text{H}_4 \cdot \text{Me} \cdot \text{N} \cdot \text{C}_{10}\text{H}_7 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ ,  
 deep violet, prismatic tablets, which can also be hydrolysed to its components, Michler's ketone, and tolyl- $\alpha$ -naphthylamine.

$\alpha$ -Naphthol-Blue (tetramethyldiaminonaphthafuchsone), the condensation product of Michler's ketone, and  $\alpha$ -naphthol, when pure, forms dark coloured prisms, m. p. 266–270°; *hydrochloride*, green needles; *platinichloride*, dark coloured. No carbinol, carbinyl ether, or carbinylamine could be isolated; it gives a green *acetyl derivative*, and on reduction in acetic acid by zinc dust a *leuco-base*,



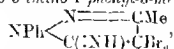
prisms, m. p. 187–188°.

Naphtho-Blue (Naefling and Philipp, *loc. cit.*), the condensation product of Michler's ketone and dimethyl- $\alpha$ -naphthylamine, can be separated into a coloured and a colourless constituent; the latter is, as

earlier suggested, the carbinol,  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NMe}_2$ , but the former is actually identical with  $\alpha$ -Naphthol-Blue, and must be produced by a partial elimination of dimethylamine during the neutralisation of the reaction product; the product also always contains some pentamethyl compound,  $\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3\cdot\text{C}_{10}\text{H}_6\cdot\text{NMe}_2\cdot\text{HCl}$ , due to a loss of a methyl group similar to that observed in the preparation of crystal-violet. For the preparation of the pure colourless carbinol of Naphtho-Blue it is advisable to use in the condensation an excess of dimethyl- $\alpha$ -naphthylamine, and then to render the solution of the product alkaline at as low a temperature as possible. Treatment of the aqueous solution of the chloride with ammonia yields the colourless carbinylamine, m. p. 173—175°. D. F. T.

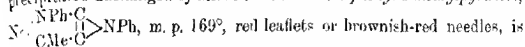
5-Aminopyrazole and Iminopyrines. III. 5-Imino 1-phenyl-3-methylpyrazolone. ARCEUR MICHAELIS and ARTHUR SCHÄFER (*Annalen*, 1913, 397, 119—148. Compare A., 1911, i, 1037; 1905, i, 476).—1-Phenyl-3-methyl 4:5-azipyrazole,  $\text{N} \begin{smallmatrix} \text{NPh}\cdot\text{C} \\ \text{CMe}\cdot\text{CH} \end{smallmatrix} \text{N}$ , m. p.

109°, yellowish brown leaflets, prepared by warming 5-amino-1-phenyl-3-methylpyrazole (5-imino 1-phenyl-3-methylpyrazolone) in 50% acetic acid with concentrated hydrogen peroxide, is converted into 5-amino-1-phenyl-3-methylpyrazole by reducing agents and into 4-halogeno-5-amino-1-phenyl-3-methylpyrazoles by warming with concentrated halogen acids. 4-Chloro-1-phenyl-3-methyl-4:5-azipyrazole, m. p. 103°, red leaflets, is obtained by treating 4-chloro-5-amino-1-phenyl-3-methylpyrazole with hydrogen peroxide as above, or, in hydrochloric acid, with concentrated sodium nitrite. It is also obtained by leading chlorine into a hydrochloric acid solution of 5-amino-1-phenyl-3-methylpyrazole. The last method has enabled the authors to explain the constitution of the trichloro-compound obtained by Michaelis and Brust (*loc. cit.*); this is not 1-chloro-5-amino-1-dichlorophenyl-3-methylpyrazole as stated previously, but 4-chloro-5-dichloroamino-1-phenyl-3-methylpyrazole, m. p. 60°, since it yields 4-chloro-1-phenyl-3-methyl-4:5-azipyrazole by warming with water. Unlike the non-halogenated compound, 4-chloro-1-phenyl-3-methyl-4:5-azipyrazole is unchanged by halogen acids; it is reduced to 4-chloro-5-amino-1-phenyl-3-methylpyrazole by boiling concentrated sodium hyposulphite. 4-Bromo-1-phenyl-3-methyl-4:5-azipyrazole,  $\text{C}_{10}\text{H}_8\text{N}_2\text{Br}$ , m. p. 101°, reddish-brown leaflets, prepared by similar methods to the chloro-compound, yields 4-bromo-5-amino-1-phenyl-3-methylpyrazole by reduction, and is converted into 4:4-dibromo-5-imino-1-phenyl-3-methylpyrazolone,



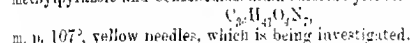
m. p. 126°, colourless needles, and 4-chloro-4-bromo-5-imino-1-phenyl-3-methylpyrazolone, m. p. 124°, colourless needles, by warming with hydrobromic acid or hydrochloric acid, and subsequently basifying with ammonia. 4-Iodo-1-phenyl-3-methyl-4:5-azipyrazole,  $\text{C}_{10}\text{H}_8\text{N}_2\text{I}$ , m. p. 154°, yellowish-red needles, prepared by the oxidation of 4-iodo-5-amino-1-phenyl-3-methylpyrazole or by heating 5-amino-1-phenyl-3-methylpyrazole with alcoholic iodine and sodium hydroxide at 150°, is

unchanged by halogen acids, and is converted into 4-iodo-5-amino-1-phenyl-3-methylpyrazole by reduction. 1-Phenyl-3:4-dimethyl-4:5-acetpyrazole,  $C_{11}H_{11}N_3$ , m. p. 105°, red leaflets, is prepared by oxidising 3-amino-1-phenyl-3:4-dimethylpyrazole in hydrochloric acid by hydrogen peroxide; it is soluble in concentrated halogen acids and is precipitated unchanged by alkalis. 4:5-Amino-1-phenyl-3-methylpyrazole,



prepared by treating a glacial acetic acid solution of 4-benzenceno-5-amino-1-phenyl-3-methylpyrazole with concentrated sodium nitrite, whereby nitrogen and nitric oxide are evolved. By reduction with tin and alcoholic hydrochloric acid, it yields benzene and 4-amino-1-phenyl-3-methyl-5-pyrazolone hydrochloride, by the oxidation of which in the air rubazonic acid is produced. 4- $\beta$ -Naphthaleneceno-5-amino-1-phenyl-3-methylpyrazole,  $C_{20}H_{17}N_3$ , m. p. 117°, yellow leaflet, prepared from  $\beta$ -naphthalenediazonium chloride and 5-amino-1-phenyl-3-methylpyrazole in aqueous sodium carbonate, is converted in a similar manner into 4:5- $\beta$ -naphthylimino-1-phenyl-3-methylpyrazole,  $C_{20}H_{15}N_3$ , m. p. 178°, reddish-brown needles, by the reduction of which naphthalene and 4-amino-1-phenyl-3-methylpyrazole are formed.

5-Formylamino-1-phenyl-3-methylpyrazole,  $C_{11}H_{11}ON_3$ , m. p. 135°, colourless needles, prepared from the aminopyrazole and formic acid on the water-bath, and the corresponding benzoylamino-derivative,  $C_{17}H_{15}ON_3$ , m. p. 113°, long needles, have been prepared; the latter is converted into 4-bromo-5-benzoylamino-1-phenyl-3-methylpyrazole, m. p. 172°, by bromine in dilute acetic acid. 5-Benzenceno-phenylamino-1-phenyl-3-methylpyrazole has m. p. 170°. 5-Acetyl-amino-1-phenyl-3-methylpyrazole and benzenediazonium chloride yield a substance,



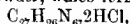
Hot aqueous potassium cyanate and 5-amino-1-phenyl-3-methylpyrazole hydrochloride yield 5-carbamido-1-phenyl-3-methylpyrazole,  $NH_2 \cdot CO \cdot NH \cdot C \begin{array}{c} \text{NPh} \cdot \text{N} \\ \text{CH} \cdot \text{CMe} \end{array}$ , m. p. 215°, colourless needles.

5-Amino-1-phenyl-3-methylpyrazole and phenylcarbimide yield, by heating, 5-phenylcarbimido-1-phenyl-3-methylpyrazole, m. p. 205°; the phenylthiocarbimido-derivative, m. p. 159°, is prepared in a similar manner. The 5-aminopyrazole and carbon disulphide at 150° yield the *s-thiocarbimide*,  $CS(NH \cdot C_{10}H_8N_2)_2$ , m. p. 184°.

5-Amino-1-phenyl-3-methylpyrazole can be almost completely diazotised in nearly concentrated hydrochloric acid (compare Mohr, A., 1909, i. 194); the solution does not contain 4-oximino-5-imino-1-phenyl-3-methylpyrazolone, and yields coloured precipitates with alkaline  $\beta$ -naphthol and resorcinol. 1-Phenyl-3-methylpyrazole-5-azoresorcinol,  $C_{15}H_{11}O_4N_5$ , yellow needles, has m. p. 250°. 1-Phenyl-3-methylpyrazole-5-diazonium chloride and 1-phenyl-3-methyl-5-pyrazolone in acetic acid slowly form 1-phenyl-3-methylpyrazole-5-(4-*pyrazol-3-methyl-5-pyrazolone*),  $N \begin{array}{c} \text{Ph} \cdot \text{C} \\ \text{CMe} \cdot \text{CH} \end{array} \text{C} \cdot \text{N}_2 \cdot \text{CH} \begin{array}{c} \text{CO} \cdot \text{NPh} \\ \text{CMe} \cdot \text{N} \end{array}$ , m. p. 175°, yellowish-red needles, which is soluble in alkalis. 5-Diazamino

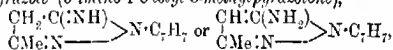
1-phenyl-3-methylpyrazole,  $C_{10}N_3H_9 \cdot N_2 \cdot NH \cdot C_{10}H_9$ , m. p. 182°, yellow leaflets, is obtained by treating 5-amino-1-phenyl-3-methylpyrazole in hydrochloric acid with less than 1 mol. of sodium nitrite, or by carefully treating the completely diazotised solution with aqueous sodium hydroxide.

5-Amino-1-phenyl-3-methylpyrazole and benzaldehyde at 135° yield 4-benzylidenebis-5-amino-1-phenyl-3-methylpyrazole,  $CHPh(C_{10}N_3H_9)_2$ , m. p. 66°, faintly yellow powder, which forms a hydrochloride,



m. p. 218° (platinichloride, yellowish-red crystals), in the cold, but is converted into its generators by hot acids. The corresponding o-nitrobenzylidene, salicylidene, and anisylidene compounds, m. p. 89°, 120°, and 219° respectively, are described. C. S.

5-Amino-1-o- and p-tolyl-3-methylpyrazoles. AUGUST MICHAELIS and LUDWIG KLAPPERT (*Annalen*, 1913, 397, 149—159).—Acetoacetonitrile-o-tolylhydrazine,  $CN \cdot CH_2 \cdot CMe : N \cdot NH \cdot C_7H_7$ , m. p. 115°, colourless needles, prepared from acetoacetonitrile and o-tolylhydrazine in 30% acetic acid, is converted, by heating with alcoholic hydrochloric acid at 120° for three hours and basifying, into 5-amino-1-o-tolyl-3-methylpyrazole (5-amino-1-o-tolyl-3-methylpyrazolone),



m. p. 93°, b. p. 314°, colourless crystals (hydrochloride, m. p. 113°), which reacts in hydrochloric acid with chlorine, in glacial acetic acid with bromine, and in alcohol with iodine, to form, after basifying, 4-chloro-5-amino-1-o-tolyl-3-methylpyrazole, m. p. 114°, and the 4-bromo-compound, m. p. 134°, and the 4-iodo-compound, m. p. 141°, respectively. By prolonged treatment with chlorine, a hydrochloric acid solution of 5-amino-1-o-tolyl-3-methylpyrazole yields 4-chloro-1-o-tolyl-3-methyl-4:5-azipyrazole,  $N \ll CMe - CCl \gg N$ , m. p. 107°, red leaflets. 4-Bromo-1-o-tolyl-3-methyl-4:5-azipyrazole, m. p. 115°, red needles, and the 4-iodo-compound, m. p. 133°, reddish brown leaflets, are prepared in a similar manner by means of bromine in acetic acid, and by alcoholic iodine at 140—150°.

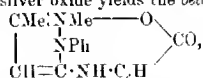
5-Amino-1-o-tolyl-3-methylpyrazole is converted into 5-acetyl-amino-1-o-tolyl-3-methylpyrazole, m. p. 157°, colourless needles, by boiling acetic anhydride, into 4-benzenearazo-5-amino-1-o-tolyl-3-methylpyrazole, m. p. 118°, yellow leaflets, by benzenediazonium chloride in hydrochloric acid and subsequent addition of sodium carbonate, into 4-oximino-5-amino-1-o-tolyl-3-methylpyrazolone, m. p. 195°, red crystals, by sodium nitrite and 30% acetic acid, and into 5-amino-1-o-tolyl-3-methylpyrazole methiodide,  $CH \ll C(NH_2) : N \cdot C_7H_7 \gg CMe = NMeI$ , m. p. 245°, colourless crystals, by boiling methyl alcoholic methyl iodide. The methiodide is changed by silver chloride to the methochloride, m. p. 241°, an aqueous solution of which yields, by treatment with concentrated sodium hydroxide, 2:5-amino-1-o-tolyl-2:3-dimethylpyrazole (1-o-tolyl-

iminopyrine),  $\text{C} \begin{array}{c} \text{CH} \cdot \text{CMe} \\ \text{---} \text{NH} \text{---} \\ \text{N}(\text{C}_7\text{H}_7) \end{array} \text{NMe}$ , m. p. 35–36°, yellow crystals, from which have been prepared the *carbonate*, m. p. 98° (decomp.), *picrate*, m. p. 165°, yellow needles, *benzenesulphonyl* derivative,

$\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}_3\text{S}$ , m. p. 179°, *benzoyl* derivative, m. p. 186°, and 4-*benzeneazo*-1-*o*-*tolyl*-*iminopyrine*,  $\text{C}_{18}\text{H}_{19}\text{N}_3$ , m. p. 188°, yellowish-brown leaflets.

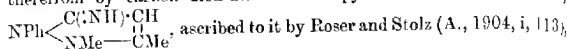
The following compounds of the para-series are prepared by methods similar to the preceding: *Acetoacetone*-trile-*p*-*tolylhydrazone*, m. p. 123°, yellow leaflets; 5-*amino*-1-*p*-*tolyl*-3-*methylpyrazole*, m. p. 120°, colourless needles; 4-*bromo*-5-*amino*-1-*p*-*tolyl*-3-*methylpyrazole*, m. p. 138°, colourless needles; 4-*bromo*-1-*p*-*tolyl*-3-*methyl*-4:5-*azipyrazole*, m. p. 103°, orange-red leaflets; 4-*oximino*-5-*imino*-1-*p*-*tolyl*-3-*methylpyrazolone*, m. p. 198°, bordeaux red crystals; 5-*amino*-1-*p*-*tolyl*-3-*methylpyrazole methiodide*, m. p. 135°, and *methochloride*; 1-*p*-*tolyl*-*iminopyrine* (*picrate*, m. p. 177°, yellow needles; *benzenesulphonyl* derivative, m. p. 203°; *carbonate*, decomp. 126°; and 4-*benzeneazo*-derivative, m. p. 191°, yellowish-brown leaflets). C. S.

**5-*p*-Carboxylic Acids of Anilopyrine and their Esters.** AUGUST MICHAELIS and WILHELM TITUS (*Annalen*, 1913, 397, 159–180).—The main object of the research is the production of further evidence in support of Michaelis's constitution for the iminopyrines. Antipyrene chloride and methyl *p*-aminobenzoate (3 mols.), heated at 130°, yield, by basifying the aqueous solution of the product, *methyl* 2:5-*anilo*-1-*phenyl*-2:3-*dimethylpyrazole*-*p*-*carboxylate* (*methyl anilopyrine*-*p*-*carboxylate*),  $\text{CMe}_2\text{N} \begin{array}{c} \text{Me} \\ | \\ \text{NPh} \\ | \\ \text{CH}=\text{C} \end{array} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$ , m. p. 155°, greenish-yellow prisms, which forms a *hydrochloride*, m. p. 142°, *platinichloride*, m. p. 200°, red crystals, *hydriodide*, m. p. 242° (decomp.), colourless needles, and *methiodide*,  $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}_3\text{I} \cdot 3\text{H}_2\text{O}$ , m. p. 102° (anhydrous, 202° [decomp.]), and is converted into the 4-*bromo*-compound,  $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_3\text{Br}$ , m. p. 170°, yellow leaflets, by bromine in acetic acid. By hydrolysing the ester with concentrated alcoholic potassium hydroxide and treating the product with hydrochloric acid and finally with aqueous potassium iodide, the *hydriodide*, m. p. 236°, colourless needles, of anilopyrine-*p*-carboxylic acid is obtained. According to the authors, it has the constitution  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C} \begin{array}{c} \text{NPh} \cdot \text{NMe} \\ | \\ \text{CH}=\text{C} \end{array} \text{Me}$ , and by treating its aqueous solution with silver oxide yields the *betains*,

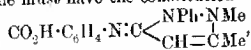


which crystallises in needles containing 5H<sub>2</sub>O, m. p. 99–100° (the anhydrous substance is yellow and has m. p. about 150°), has a neutral reaction in dilute aqueous or alcoholic solution and a distinctly alkaline reaction in concentrated solution, does not form salts

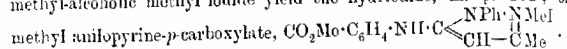
with bases, but does so readily with acids (*hydrochloride*,  $C_{18}H_{17}O_2N_3$ ,  $HCl$ ; *platinechloride*,  $2C_{18}H_{17}O_2N_3 \cdot H_2PtCl_6$ , m. p.  $217^\circ$ , golden-yellow crystals), and, although soluble in aqueous alkalis, is precipitated therefrom by carbon dioxide. If iminopyrine has the constitution,



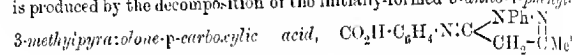
ascribed to it by Roser and Stolz (A., 1904, i, 113), the preceding betaine must have the constitution



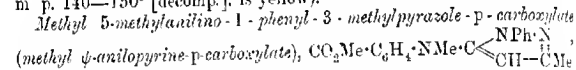
and therefore should exhibit acid properties. The betaine and methyl-alcoholic methyl iodide yield the hydriodide, m. p.  $212^\circ$ , of



By evaporating a hydrochloric acid solution of methyl anilopyrine-*p*-carboxylate and heating the residue under reduced pressure, methyl chloride is evolved, and the product, after treatment with sodium hydroxide, yields 5-anilo-1-phenyl-3-methylpyrazolone. This substance is produced by the decomposition of the initially-formed 5-anilo-1-phenyl-



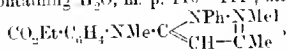
colourless needles containing  $H_2O$ , m. p.  $111^\circ$  (the anhydrous substance, m. p.  $140\text{--}150^\circ$  [decomp.], is yellow).



m. p.  $132^\circ$ , colourless needles, is obtained by heating the methiodide of methyl anilopyrine-*p*-carboxylate at  $200^\circ$  under reduced pressure. It is converted into the 4-nitroso-compound,  $C_{19}H_{15}O_2N_3$ , m. p.  $151^\circ$ , pale green leaflets, by sodium nitrite and glacial acetic acid containing a few drops of hydrochloric acid, into the 4-nitro-compound,  $C_{19}H_{15}O_2N_4$ , m. p.  $170^\circ$ , pale yellow needles, by nitric acid, into a dibromo-derivative,  $C_{19}H_{17}O_2N_3Br_2$ , m. p.  $115^\circ$ , by bromine on the water-bath, and into the corresponding acid,  $C_{18}H_{17}O_2N_3$ , m. p.  $193^\circ$ , by hydrolysis. This acid is isomeric with the betaine mentioned previously, but exhibits pronounced acid reaction and properties, being soluble in dilute alkali hydroxides and carbonates and in ammonia; the crystalline barium salt,  $Ba(C_{18}H_{17}O_2N_3)_2$ , is described.

Ethyl 2:5-anilo-1-phenyl-2:3-dimethylpyrazole-*p*-carboxylate (ethyl anilopyrine-*p*-carboxylate),  $C_{20}H_{19}O_2N_3$ , m. p.  $76^\circ$ , greenish-yellow, fluorescent crystals, is prepared in the same manner as the methyl ester. It forms a hydriodide,  $CO_2Et \cdot C_6H_4 \cdot NH : C \begin{array}{c} \diagup NPh \cdot NMeI \\ \diagdown CH - CMe \end{array}$ ,

yellow crystals containing  $H_2O$ , m. p.  $110\text{--}111^\circ$ , methiodide,



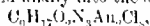
colourless crystals containing  $3H_2O$ , m. p.  $80^\circ$  (anhydrous,  $183^\circ$ ), and ethiodide,  $C_{20}H_{19}O_2N_3I$ , m. p.  $175^\circ$ , colourless needles, and by hydrolysis yields the same betaine as the methyl ester.

By heating the methiodide of the ethyl ester at  $160\text{--}180^\circ$  under re-

duced pressure, *ethyl 5-methylavilino-1-phenyl-3-methylpyrazole-p-carboxylate* (ethyl  $\psi$ -anilopyrine-p-carboxylate),  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{C} \begin{smallmatrix} \text{NPh} \\ \text{N} \\ \text{CH} - \text{CMe} \end{smallmatrix}$ , m. p. 105°, colourless needles, is obtained, by the hydrolysis of which  $\psi$ -anilopyrine-p-carboxylic acid, m. p. 193°, is obtained.

In a similar manner the ethiodide of the ethyl ester yields *ethyl 5-ethylavilino-1-phenyl-3-methylpyrazole-p-carboxylate*, m. p. 95°, colourless needles. C. S.

**Synthesis of Herzynine.** R. ENGELAND and FRIEDRICH KUTSCHER (*Chem. Zentr.*, 1913, i, 28—29; from *Zentr. Physiol.*, 1912, 26, 569—570. Compare A., 1911, ii, 528).—The substance,  $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}_3$ , which was isolated from mushrooms in the form of the aurichloride, has been identified with trimethylhistidine. This base is prepared by treating histidine hydrochloride in concentrated hydrochloric acid with silver nitrite and warming the syrup obtained by evaporating the filtrate with an alcoholic solution of trimethylamine, when the base is precipitated by phosphotungstic acid, converted into the chloride, then into the platinochloride, and finally into the *aurichloride*,



m. p. 183° (decomp.). The direct methylation of histidine affects the glyoxaline ring, and, under certain conditions, a good yield of *penta-methylhistidine* may be obtained as an unstable base which forms a stable chloride and a sparingly soluble *aurichloride*,  $\text{C}_{11}\text{H}_{21}\text{O}_2\text{N}_5\text{Au}_2\text{Cl}_3$ , m. p. 220°, but does not respond to the diazo-reaction. J. C. W.

**The Identity of Trimethylhistidine (Histidine-betaine) from Various Sources.** GEORGE BARGER and ARTHUR J. EWINS (*Biochem. J.*, 1913, 7, 204—206).—Proof is given of the identity of the histidine-betaine described by the author (C., 1911, 99, 2336) with the compounds obtained by Reuter and Kutschner. The difference in the m. p. given for the dipicrate is due to this substance melting at 123—124° when hydrated ( $2\text{H}_2\text{O}$ ) and at 205—206° when anhydrous. The dipicrate has m. p. 213°; the monopicrate, m. p. 201—202°. The aurichloride of betaine has m. p. 184°, not at 171° as previously stated. Histidine-betaine has  $[\alpha]_D + 46.5$ . W. D. H.

**Synthetic Alkaloids from Tyrosine, Tryptophan and Histidine.** JULIUS WELLSCH (*Biochem. Zeitsch.*, 1913, 49, 173—194).—The author discusses the mechanism of the various processes by means of which physiologically active bases can be synthesised in plants, especially from amino-acids which can be derived from the hydrolysis of proteins. Amongst these may be reckoned in the first instances, bases such as 3- $\beta$ -aminoethylglyoxaline, 3- $\beta$ -aminoethylindole, and phenylethylamine, which are derived from histidine, tryptophan, and phenylalanine by the simple scission of carbon dioxide. Another important series derivable from these amino-acids are the quinoline and pyridine derivatives, which can be obtained from the acids or the corresponding amines by condensation with aldehydes, such as formaldehyde, and subsequent ring formation. Attempts have been



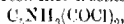
made to prepare a series of alkaloids by the latter method. By the condensation of histidine with formaldehyde, which was carried out by heating the base with methylal and hydrochloric acid, *tetrahydro-1:3:5-benzotriazole-6-carboxylic acid*,  $C_7H_9N_3O_2 \cdot 2HCl$ , in the form of its hydrochloride, m. p.  $278^\circ$  (corr.), was obtained. The *picrate* decomposes about  $215^\circ$ . The hydrochloride is laevorotatory ( $[\alpha]_D^{25} = -84.24^\circ$  by the micropolarisation method). On heating in a vacuum to  $290^\circ$ , carbon dioxide is evolved, and the corresponding *iminazole*, isopiperidine [*tetrahydro-1:3:5-benzotriazole*] *hydrochloride*,  $C_6H_9ON_3 \cdot 2HCl$ ,

which decomposes at  $258^\circ$ , was obtained, and which separates from alcohol in a microcrystalline form. The carboxylic acid cannot be esterified by alcohol and hydrochloric acid, and only with very great difficulty by the action of ethyl iodide on the silver salt. Attempts were made to obtain a corresponding product by the action of methylal on tryptophan, but a pure substance was not isolated. *L*-Tyrosine under similar conditions gives 7-hydroxytetrahydroisoquinoline-3-carboxylic acid (Pictet and Spengler, A., 1911, i, 750), which has  $[\alpha]_D^{25} = -45.62^\circ$  in hydrochloric acid. This on heating in a vacuum appears to be converted into an anhydride. The *ethyl* ester and its *picrate* were also prepared. Attempts to condense histidine with acetaldehyde and pyruvic acid did not lead to the isolation of pure products.

S. B. S.

**Derivatives of *isoCinchomeronic Acid* and 2:5-Diaminopyridine.** HANS MEYER and FRIEDRICH STAFFEN (*Monatsh.*, 1913, 34, 517—533).—Very few derivatives of *isocinchomeronic acid* (pyridine-2:5-dicarboxylic acid) have been described (compare Weidel and Hezig, A., 1886, 477; Meyer, A., 1903, i, 364).

*isoCinchomeronic acid* was obtained for this investigation by the condensation of aldehyde ammonia with twice its weight of paraldehyde in an autoclave at  $220$ — $230^\circ$ , and oxidation of the resultant 2:5-methylethylpyridine with the theoretical amount of potassium permanganate. The m. p. of the acid can be raised from  $237^\circ$  to  $254^\circ$  (decomp.) by conversion into the methyl ester and regeneration; ammonium salt, m. p.  $153^\circ$ . If the acid is heated with excess of thionyl chloride, it is converted into *isocinchomeronyl chloride*,



needles, m. p.  $59^\circ$ , which reacts with methyl alcohol in the cold, producing *methyl isocinchomeronate*, needles, m. p.  $164^\circ$ , which is also obtainable by heating a mixture of the acid and alcohol with sulphuric acid at  $100^\circ$ . The acid chloride in the cold and the methyl ester at  $100^\circ$  react with ammonia solution, forming *isocinchomeronamide*,  $C_5NH_2(CO \cdot NH_2)_2$ , colourless crystals, m. p.  $310^\circ$  (decomp.). When boiled in alcoholic solution with an equal weight of hydrazine hydrate, methyl *isocinchomeronate* is converted into a crystalline solid, from which chloroform extracts the *methyl* ester of *isocinchomeronic acid hydrazide*,  $C_5NH_2(CO_2Me) \cdot CO \cdot NH \cdot NH_2$ , yellow scales, m. p.  $173^\circ$  (decomp.), whilst the undissolved residue consists of *isocinchomeronic hydrazide*,  $C_5NH_2(CO \cdot NH \cdot NH_2)_2$ , prismatic needles, m. p.  $268$ — $269^\circ$ .

(decomp.), with rapid heating, which is obtained in almost theoretical yield if twice the above proportion of hydrazine hydrate be used in the preparation. The dihydrazide condenses with various aldehydes when heated with them, or when shaken in aqueous solution with them; *isocinchomeronodibenzylidenedihydrazide*, colourless needles, m. p.  $296^{\circ}$ ; *isocinchomeronodi-o-chlorobenzylidenedihydrazide*, colourless leaflets, m. p.  $308^{\circ}$  (decomp.); *isocinchomeronodi-1-hydroxy-3-methoxybenzylidenedihydrazide*, a yellow, crystalline substance, m. p.  $264-266^{\circ}$ , which is turned red on the addition of mineral acids. An aqueous solution of the dihydrazide containing the theoretical quantity of hydrochloric acid reacts with sodium nitrite, giving a precipitate of *isocinchomeronodiazoinide*,  $C_5NH_3(CO \cdot N_3)_2$ , colourless prisms, m. p.  $114^{\circ}$  (decomp. with explosion), together with a small amount of an acid substance, a colourless, crystalline powder, m. p.  $307^{\circ}$  (decomp.), which from its reaction with ferrous sulphate is a 2-substituted pyridine derivative. The carefully-dried hydrazide when boiled with alcohol first dissolves and then gives a deposit of *ethylurethylpyridylazoinide*,

$N_3 \cdot CO \cdot C_5NH_3 \cdot NH \cdot CO_2Et$ ,  
colourless needles, m. p.  $153^{\circ}$  (with explosion), which by prolonged treatment with boiling alcohol is further converted into 2:5-diethylurethylpyridine,  $C_5NH_3(NH \cdot CO_2Et)_2$ , colourless needles, m. p.  $198-199^{\circ}$ , the ethoxyl groups of which, unlike those of the corresponding derivative of dipicolinic acid, are easily removed by hydriodic acid. The corresponding *methylurethylpyridylazoinide*,

$N_3 \cdot CO \cdot C_5NH_3 \cdot NH \cdot CO_2Me$ ,  
and 2:5-dimethylurethylpyridine form colourless needles (which explode at  $80-100^{\circ}$  if rapidly heated, and melt at above  $270^{\circ}$  with decomp. if heated slowly) and colourless needles, m. p.  $206-207^{\circ}$  (decomp.) respectively.

If the above diethylurethylpyridine is boiled for three hours with hydriodic acid (D 1.8-1.9), yellow needles and leaflets of the *hydriodide* of 2:5-diaminopyridine separate on cooling; the free base, colourless needles, m. p.  $107-110^{\circ}$ , which is rapidly affected by air and light, can be isolated by triturating the hydriodide with crushed potassium carbonate and carefully extracting with hot benzene in an atmosphere of carbon dioxide. By the action of silver chloride the hydriodide is converted into the *hydrochloride*, colourless needles, which, like the free base, gives solutions in water and alcohol with a blue fluorescence; the unstable *platinichloride* crystallises in golden-yellow scales; *benzoyl* derivative, colourless needles, m. p.  $229-230^{\circ}$ . The base does not possess the usual properties of an aromatic diamine; it gives an intense reddish-yellow coloration with ferric chloride, and the hydrochloride reduces gold solutions and ammoniacal silver solutions.

D. F. T.

**Preparation of Acylacetic Esters.** ANDRÉ WAHL and M. DOLL (*Bull. Soc. chim.*, 1913, [iv], 13, 265-281. Compare A., 1911, i, 198).—The authors have continued their previous work on the condensation of ethyl acetate with its higher homologues by means of sodium, and have improved the yields by suitable modification of the

procedure, which is fully described. They have also extended the method to the cases of ethyl valerate and ethyl heptate, and find that the yield of ketonic ester increases with increasing length of the carbon chain of the ester provided the latter is normal. With esters having side-chains, condensation is effected with greater difficulty.

Ethyl propionylacetate has now been obtained in 13% yield. It forms a green copper salt, m. p. 144°.

Ethyl butyrylacetate is readily converted into ethyl isonitrosobutyrylacetate, which did not solidify even after several months and could not be distilled without decomposition. Phenylhydrazine converts it into 4-oximino-1-phenyl-3-propyl-5-pyrazolone, yellow needles, m. p. 128°. When acted on by benzenediazonium chloride, ethyl butyrylacetate is converted into a yellow oil, which is identified as ethyl phenylazobutyrylacetate, since it is converted by phenylhydrazine into 4-phenylhydrazino-1-phenyl-3-propyl-5-pyrazolone,  $\text{NPh} \begin{smallmatrix} \text{CO} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{C} \\ \text{N} \end{smallmatrix} \text{NHPh}$ ,

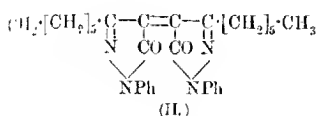
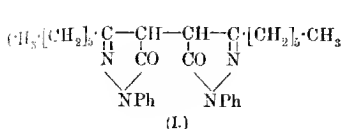
orange needles, m. p. 133–134°, and by p-nitrophenylhydrazine into 4-phenylhydrazino-1-p-nitrophenyl-3-propyl-5-pyrazolone, golden-yellow needles, m. p. about 209–210°. Ethyl p-nitrophenylazobutyrylacetate crystallises in fine yellow needles, m. p. 101°, whilst the corresponding acid, prepared by saponification of the ester with cold alcoholic sodium hydroxide and subsequent addition of acid, forms yellow crystals, m. p. 164°. 4-p-Nitrophenylhydrazino-1-phenyl-3-propyl-5-pyrazolone,  $\text{NPh} \begin{smallmatrix} \text{CO} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{C} \\ \text{N} \end{smallmatrix} \text{NH} \cdot \text{C}_6\text{H}_4\text{NO}_2$ , red needles, m. p. 194°, 4-p-nitrophenylhydrazino-1-p-nitrophenyl-3-propyl-5-pyrazolone, orange needles, m. p. 213–244°, and 4-p-nitrophenylhydrazino-1-tolyl-3-propyl-5-pyrazolone, orange needles, m. p. 152°, were also prepared.

Ethyl valerylacetate,  $\text{CH}_3\text{Pr} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{Et}$ , b. p. 110–112°/16 mm. (compare Blaise and Luttringer, *Bull. Soc. chim.*, 1905, [iii], 33, 1103), is obtained in 28% yield. It gives a copper salt, green needles, m. p. 91°, which, when boiled with methyl alcohol, is converted into a blue basic salt,  $\text{C}_9\text{H}_{11}\text{O}_3 \cdot \text{CuOMe}$ , m. p. 80°. It is transformed by hydrazine hydrate into 3-n-butyrylpyrazolone, white leaflets, m. p. 197°.

Ethyl isovalerate reacts slowly with ethyl acetate with the formation of poor yields of ethyl isovalerylacetate, b. p. 96–99°/14 mm. The latter gives a green normal copper salt, m. p. 122°, which when boiled with methyl alcohol forms indigo-blue crystals of the basic salt,  $\text{C}_{11}\text{H}_{13}\text{O}_3 \cdot \text{CuOMe}$ ,

m. p. 106–107°.

Ethyl heptylacetate, b. p. 123–126°/11 mm. (compare Mourou and Delange, A., 1903, i, 676), is obtained in 40% yield by the condensation of ethyl heptate with ethyl acetate. The following new compounds have been prepared from it: 4-phenylhydrazino-1-phenyl-3-hexyl-5-pyrazolone, orange-yellow needles, m. p. 100–101°; 4-p-nitrophenylhydrazino-1-p-nitrophenyl-3-hexyl-5-pyrazolone, orange needles, m. p. 192°; 1-phenyl-3-hexyl-5-pyrazolone, nearly white leaflets, m. p. 83–84°. formed by heating at its b. p. for a few moments an acetic acid solution of molecular quantities of the ketonic ester and phenylhydrazine. If



in the latter case 2 to 3 molecules of phenylhydrazine are employed for each molecule of ketonic ester, 1-phenyl-3-hexylthiopyrazolone (formula I), crystalline powder, m. p. 276—278° (decomp.), is obtained, which, when heated in alkaline solution with sodium nitrite and subsequently acidified,

yields the compound (formula II) crystallising in blue needles, m. p. 115°.

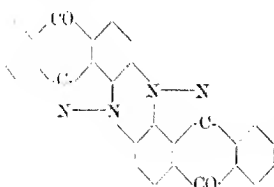
The method has also been successfully applied to certain cyclic esters. Ethyl benzoate and ethyl acetate gave ethyl benzoylacetate in 80% yield (compare Wahl, A., 1908, i, 647; Wahl and Silberzweig, A., 1912, i, 114), whilst the corresponding methyl ester gave an 85% yield of methyl benzoylacetate. Propyl benzoylacetate, prepared by boiling methyl benzoylacetate with propyl alcohol in a fractionating apparatus so arranged that the displaced methyl alcohol slowly distils, forms an amber liquid, b. p. 154—156°/12 mm., D<sub>4</sub> 1.114. The normal copper salt forms green leaflets, m. p. 145—146°, whilst the basic salt, C<sub>11</sub>H<sub>13</sub>O<sub>3</sub>·CuOMe, consists of blue crystals, m. p. 195°.

The normal green copper salt, m. p. 133°, of isobutyl benzoylacetate is decomposed by boiling methyl alcohol with formation of the bluish-grey basic salt, C<sub>13</sub>H<sub>15</sub>O<sub>3</sub>·CuOMe, m. p. 191°; and by boiling ethyl alcohol into the blue basic salt, C<sub>13</sub>H<sub>15</sub>O<sub>3</sub>·CuOEt, m. p. 188°.

Under the conditions used in the preparation of the benzoylacetates, a 60% yield of methyl *o*-methoxybenzoylacetate and a 62% yield of methyl anisoylacetate were obtained. The yield of ethyl furoylacetate was 76% of the theoretical (compare Torrey and Zanetti, A., 1907, i, 146; 1908, i, 840; 1910, i, 892).

II. W.

#### [Preparation of an Anthracene Derivative.]



CHERMISCHE FABRIK GRIESHEIM - ELEKTRO (D.R.P. 255641).—The compound (annexed formula) is obtained when pyrazoleanthrone (A., 1906, i, 304) is boiled with potassium hydroxide (5 parts) and alcohol (10 parts) until the so-obtained blue colour ceases to gain intensity.

E. M. G. M.

New Derivatives of Azoxybenzene. ANGELO ANGELI and BRUNO VIGORI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 132—140. Compare A., 1912, i, 321).—*p*-Azobenzencarboxylic acid (which has m. p. 241°)

VOL. CIV. i.

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is conveniently prepared from *p*-aminobenzoic acid and nitrosobenzene. When it is treated in acetic acid solution with hydrogen peroxide, *β*-azoxybenzenecarboxylic acid,  $\text{NPh}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , is obtained; it crystallises in yellow needles, m. p.  $241^\circ$ . Its *ethyl* ester,  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}_2$ , has m. p.  $68^\circ$ . The acid yields *p*-azobenzene-carboxylic acid on reduction. When it is treated with bromine in the presence of iron filings, *p*-bromo-*β*-azoxybenzenecarboxylic acid,  $\text{C}_{13}\text{H}_9\text{O}_3\text{N}_2\text{Br}$ , is produced; it is a yellowish-white, crystalline powder, m. p.  $280^\circ$ . The *ethyl* ester of this acid,  $\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}_2\text{Br}$ , has m. p.  $114^\circ$ . When *β*-azoxybenzenecarboxylic acid is nitrated in glacial acetic acid solution, *p*-nitro-*β*-azoxybenzenecarboxylic acid,  $\text{C}_{13}\text{H}_9\text{O}_5\text{N}_3$ , is obtained as a yellow, crystalline powder, m. p. about  $260^\circ$  with evolution of gas. If kept for an hour on the water-bath with excess of concentrated sulphuric acid, *β*-azoxybenzenecarboxylic acid undergoes rearrangement, yielding 4-hydroxyazobenzene-4'-carboxylic acid,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , which forms red crystals, m. p.  $266^\circ$  (decomp.).

*α*-Azoxybenzenecarboxylic acid,  $\text{O}\cdot\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , is formed in the preparation of the *β*-acid, and can be separated from it by reason of its greater solubility in acetic acid. It is also obtained by the action of chromic acid on the *β*-compound. It forms pale yellow scales, m. p.  $231^\circ$ . Its *ethyl* ester,  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}_2$ , has m. p.  $77.5^\circ$ . The *α*-acid is not acted on by bromine. On reduction with aluminium amalgam, it yields *p*-azobenzene-carboxylic acid.

*β*-1-Azoxybenzenesulphonic acid,  $\text{C}_{12}\text{H}_9\text{O}_4\text{N}_2\text{S}$ , prepared by the action of hydrogen peroxide on *p*-azobenzene-sulphonic acid, forms pale yellow needles, m. p.  $144^\circ$ . The *silver* salt,  $\text{C}_{12}\text{H}_9\text{O}_4\text{N}_2\text{S}\text{Ag}$ , crystallises in lustrous laminae. The acid described under the name of *p*-azoxybenzene-ulphonic acid by Limpricht (A., 1885, 981) cannot have this structure. *β*-*p*-Azoxybenzenesulphonic acid yields a bromo-derivative, *p*-bromo-*β*-azoxybenzenesulphonic acid,  $\text{C}_{12}\text{H}_9\text{O}_4\text{N}_2\text{SBr}$ , which does not melt at  $280^\circ$ . *β*-*p*-Azoxybenzenesulphonic acid suffers the Wulff rearrangement, yielding a red, crystalline powder,  $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_2\text{S}$ , which blackens about  $200^\circ$ , but does not melt.

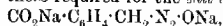
*α*:2:4:6-Trinitroazoxybenzene,  $\text{O}\cdot\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ , is obtained in long, pale yellow needles, m. p.  $170^\circ$ , by the action of hydrogen peroxide on trinitroazobenzene. This substance dissolves unaltered in nitric acid (D 1.45) and in bromine, but when it is dissolved in nitric acid of D 1.52, and the solution kept for twelve hours, it yields a tetranitro-derivative,  $\text{C}_{13}\text{H}_6\text{O}_9\text{N}_6$ , which forms yellow prisms, m. p.  $192^\circ$ .

R. V. S.

Diazo-compounds derived by the Action of Alkali on Nitrosophthalimidine. Simplified Preparation of Nitrosophthalimidine. ALFRED OPPE (*Ber.*, 1913, 46, 1095—1099).—Aqueous alkali transforms nitrosophthalimidine into *o*-hydroxymethylbenzoic acid or its lactone (Graebe, A., 1889, 140), diazo-compounds being probably formed as intermediate products. The isolation of the latter has been accomplished by substituting absolute methyl alcoholic sodium methoxide for aqueous alkali hydroxide in opening the lactam ring.

When a solution of sodium methoxide in absolute methyl alcohol

is added to a well-cooled suspension of nitrosophthalimidine in dry ether, a micro-crystalline salt separates, analysis of which gives results intermediate between those required for the *salt diazoxide*,



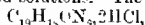
and the *ester diazoxide*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}_2\cdot\text{ONa}$ . The former could be obtained in the pure state by pouring the freshly-prepared reaction mixture into a large quantity of cooled ether, but the latter could not be obtained pure. When the above reaction mixture is treated with dry carbon dioxide before the separation of crystals occurs, *methyl o-diazomethylbenzoate*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}_2$ , needles, m. p.  $34^\circ$ , is obtained, which is readily decomposed by phenol with quantitative evolution of nitrogen and formation of *methyl o-phenoxy-methylbenzoate*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OPh}$ , needles, m. p.  $52.5^\circ$ , b. p.  $204/13$  mm. The corresponding free *acid* crystallises in needles, m. p.  $126^\circ$ , and is decomposed by fuming hydrochloric acid at  $170$ – $180^\circ$  into phenol and *o*-hydroxymethylbenzoic acid. The latter is converted by heat into phthalide, leaflets, m. p.  $73^\circ$ .

The following process is recommended for the preparation of nitrosophthalimidine. Nearly boiling 25% hydrochloric acid is gradually added to a paste made by grinding phthalimide and zinc dust with a small quantity of water. The mixture is maintained at its boiling point until there is no further action on the zinc, filtered, cooled, and treated with a concentrated aqueous solution of sodium nitrite. In this manner, 100 grams of phthalimide yield 75 grams of nitrosophthalimidine.

H. W.

**Etherification of *o*-Hydroxyazo-compounds. II.** G. CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1913–13, **48**, 539–556. Compare A., 1912, i, 812).—1-Benzeneazo-2-naphthyl ethyl ether,  $\text{OEt}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{NPh}$ , forms garnet-red tablets, m. p.  $79^\circ$ ; in its preparation 50% potassium hydroxide is used instead of 30% sodium hydroxide. When the substance is reduced with zinc and acetic acid, aniline and 1-amino-2-naphthyl ethyl ether are produced. The *hydrochloride*,  $\text{C}_{10}\text{H}_6\text{ON}_2\cdot 2\text{HCl}$ , crystallises in heavy, green leaflets, which have a metallic lustre. The *hydrobromide* is a coffee coloured, crystalline powder. The *hydriodide* is a heavy, dark coffee-coloured, crystalline powder.

1-*o*-Tolueneazo-2-naphthyl ethyl ether,  $\text{OEt}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in garnet-red, flattened needles, m. p.  $56^\circ$ . It dissolves in concentrated sulphuric acid, giving a red coloration, and dissolves also in dilute acids, forming red solutions. The *hydrochloride*,



crystallises in needles with a green, metallic lustre.

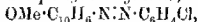
1-*m*-Tolueneazo-2-naphthyl methyl ether,  $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , forms garnet-red, tabular crystals, m. p.  $81^\circ$ . The *hydrochloride* forms minute, red crystals with a golden lustre.

1-*m*-Tolueneazo-2-naphthyl ethyl ether,  $\text{OEt}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in red leaflets, m. p.  $84^\circ$ . The *hydrochloride* is a heavy, coffee coloured substance.

1-*p*-Tolueneazo-2-naphthyl ethyl ether,  $\text{OEt}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , crys-

tallises in red, prismatic needles, m. p. 48°. The *hydrochloride*,  $C_{10}H_{15}ON \cdot 2HCl$ , forms reddish-brown needles with a golden lustre.

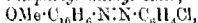
1-m-Chlorobenzeneazo-2-naphthyl methyl ether,



crystallises in bright red prisms or needles, m. p. 77°. The *hydrochloride* forms red needles.

1-m-Chlorobenzeneazo-2-naphthyl ethyl ether,  $OEt \cdot C_{10}H_6 \cdot N \cdot N \cdot C_6H_4Cl$ , forms red needles, m. p. 35°. The *hydrochloride* forms dark garnet-red crystals with a golden lustre.

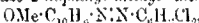
1-p-Chlorobenzeneazo-2-naphthyl methyl ether,



crystallises in shining red needles, m. p. 65°. The *hydrochloride*,  $C_{11}H_{16}ON \cdot Cl \cdot 2HCl$ , is a red, crystalline substance.

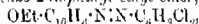
1-p-Chlorobenzeneazo-2-naphthyl ethyl ether,  $OEt \cdot C_{10}H_6 \cdot N \cdot N \cdot C_6H_4Cl$ , crystallises in red needles with a golden lustre, m. p. 53°. The *hydrochloride* is a reddish-brown, crystalline powder.

1-op-Dichlorobenzeneazo-2-naphthyl methyl ether,



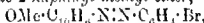
forms garnet-red leaflets, m. p. 98°. The *hydrochloride* is a red, crystalline powder having a metallic lustre.

1-op-Dichlorobenzeneazo-2-naphthyl ethyl ether,



separates in garnet-red needles, m. p. 102°. The *hydrochloride* forms minute, reddish-brown crystals with a metallic lustre.

1-m-Bromobenzeneazo-2-naphthyl methyl ether,

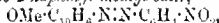


crystallises in ruby-red needles, m. p. 32°. The *hydrochloride* is a red, crystalline substance having a metallic lustre.

1-m-Bromobenzeneazo-2-naphthyl ethyl ether,  $OEt \cdot C_{10}H_6 \cdot N \cdot N \cdot C_6H_4Br$ , forms crusts of golden-yellow needles, m. p. 52°. The *hydrochloride* crystallises in metallic-looking, green leaflets.

The m. p. of 1-p-methoxybenzeneazo-2-naphthylethylether is 55–56°, not 52–53°, as stated in the former paper. The *hydrochloride* of the ether is a reddish-brown, crystalline powder having a green metallic lustre.

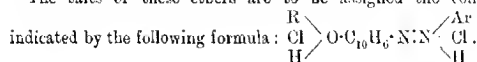
1-m-Nitrobenzeneazo-2-naphthyl methyl ether,



crystallises in small, red needles, m. p. 94–95°. The *hydrochloride* is a red, crystalline substance, as also is the *hydrobromide*.

1-m-Nitrobenzeneazo-2-naphthyl ethyl ether,  $OEt \cdot C_{10}H_6 \cdot N \cdot N \cdot C_6H_4NO_2$ , forms garnet-red needles, m. p. 106–107°. The *hydrochloride* is a red, crystalline powder.

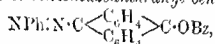
The salts of these ethers are to be assigned the constitution



R. V. S.

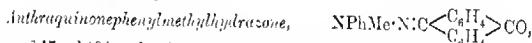
**Hydroxyazo-compounds and Quinonephenylhydrazones of the Anthracene Series.** KURT H. MEYER and KARL ZAHN (*Annalen*, 1913, 396, 152–166).—Benzeneazoanthranol, identical with the substance obtained by Kautler and Suchanek by the con-

condensation of benzenediazonium chloride and anthranol, is prepared by treating 9:9-dibromoanthrone with alcoholic phenylhydrazine; only the one substance is produced at  $-10^\circ$  or at the b. p., or by working in other solvents. The same substance also is immediately recovered when the deep blue solution of benzeneazoanthranol in alcoholic potassium hydroxide is added to sulphuric acid at  $0^\circ$ . No evidence of the existence of the parent substance as anthraquinonephenylhydrazone has been obtained. Benzeneazoanthranol yields differently coloured solutions in different solvents, develops a deep brown coloration with concentrated sulphuric acid, forms coloured additive compounds with stannic chloride and aluminium chloride, reacts instantly with alcoholic bromine, and is stable to boiling acetic acid; it is hydrolysed by 5% alcoholic sulphuric or hydrochloric acid after boiling for seven hours. All these properties, except variability of colour in solution, are also characteristic of benzeneazoanthranyl benzoate,



m. p.  $230-231^\circ$ , dark red crystals with a metallic lustre, which is prepared by treating benzeneazoanthranol in acetone with aqueous sodium hydroxide and benzoyl chloride in the cold; by prolonged boiling with alcoholic hydrochloric acid, it yields benzoic acid, anthraquinone, and phenylhydrazine. On the contrary, anthraquinonebenzoylphenylhydrazone,  $\text{NPhBz}\cdot\text{N}\cdot\text{C}\left\langle\begin{smallmatrix}\text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4\end{smallmatrix}\right\rangle\text{CO}$ , m. p.  $172-173^\circ$ , orange-

yellow prisms, prepared by heating 9:9-dibromoanthrone, alcoholic benzoylphenylhydrazine and sodium carbonate, develops a yellow coloration with concentrated sulphuric acid, does not form additive compounds with metallic chlorides, is only slowly attacked by alcoholic bromine, and is rapidly hydrolysed by boiling dilute acetic acid. It cannot be transformed into benzeneazoanthranyl benzoate by ether and powdered potassium hydroxide.



m. p.  $147-148^\circ$ , red prisms with metallic lustre, is obtained by heating 9:9-dibromoanthrone with alcoholic *as*-phenylmethylhydrazine or by treating benzeneazoanthranol in aqueous acetone with sodium hydroxide and methyl sulphate. It is not affected by alcoholic potassium hydroxide, but is hydrolysed to anthraquinone and *as*-phenylmethylhydrazine by boiling dilute acetic acid or alcoholic hydrochloric acid. It is thus seen that the acylation of benzeneazoanthranol in alkaline solution is a process of direct substitution (an *O*-ester being formed), whilst the alkylation is a case of addition followed by elimination (an *N*-ether being formed).

At the present time aliphatic hydroxyazo-compounds, such as phenylazooxyacetone, are generally regarded as hydrazones, for example,  $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{COMe})_2$ , because they yield *N*-esters  $[\text{NBzPh}\cdot\text{N}\cdot\text{C}(\text{COMe})_2]$  by acylation. The evidence is by no means conclusive, however, because the hydroxyazo-compound can yield the *N*-ester as follows:

$$\text{O}\cdot\text{S}\cdot\text{C}(\text{Me})\cdot\text{C}(\text{N}\cdot\text{NPh})\cdot\text{COMe} \xrightarrow[\text{C}]{\text{NaO}} \text{CMe}\cdot\text{C}(\text{N}\cdot\text{NBzPh})\cdot\text{COMe}$$

$\rightarrow \text{NBzPh}\cdot\text{N}\cdot\text{C}(\text{COMe})_2$ . The colour, solubility in aqueous alkalis,



and reactivity with alcoholic bromine are all in harmony with the formulation of aliphatic hydroxyazo-compounds as hydroxyazo-compounds.

Anthraquinoneoxime is obtained by treating 9:9-dibromoanthrone with alcoholic hydroxylamine and dry sodium carbonate. The same substance is at once precipitated when its alkaline solution is acidified with sulphuric acid at 0°; nitrosoanthranol is not isolated. C. S.

**Action of Acids on Proteins.** D. CĂLUGĂREANU (*Bull. Acad. Sci. Roumaine*, 1912/13, 1, 40—42).—With the object of deciding whether the products of the action of acids on proteins are chemical compounds which are hydrolytically dissociated in aqueous solution, or are simply adsorption products, the author has studied the electrical conductivity of a number of acids (hydrochloric, sulphuric, chromic, acetic, citric, lactic, trichloroacetic, and picric) at different dilutions in aqueous solution, on the one hand, and in aqueous solution in the presence of various proteins (serum-albumen, serum-globulin, and gelatin) on the other, the experimental conditions being so chosen that the concentration of the protein remains constant, the concentration of acid alone varying.

Since the curves obtained are closely similar to that given by a solution of glycine under similar conditions, the author is led to the conclusion that the form of the curve is largely due to the hydrolytic dissociation of the product of the action of acids on the protein. He does not consider, however, that the phenomenon of adsorption is completely excluded. H. W.

**The Relations of the Phenols and their Derivatives to Proteins. Mechanism of Disinfection. II. Effects of Various Factors on the Germicidal and Protein-precipitating Powers of the Phenols.** EVELYN A. COOPER (*Biochem. J.*, 1913, 7, 175—185. Compare A., 1912, ii, 1199).—The introduction of hydroxyl groups decreases, and of nitro- or methyl groups, increases, the bactericidal and protein-precipitating powers of phenol. The monohydric phenols are superior to the alcohols in both directions. Sodium chloride increases both properties through increasing the solubility of phenols in proteins; alcohol behaves in the opposite way. Solutions of phenol in fat possess no such activities. Small amounts of alkali inhibit the power to precipitate proteins, without affecting the germicidal power; the explanation of this is not apparent. The precipitating action of phenol is increased by the addition of acids. The absorption of phenols by bacteria is the initial stage in disinfection; the germicidal action is not due to a union of the phenols with the bacterial protoplasm (as with formaldehyde), but to a denaturing action upon the colloidal suspension of some constituent protein or proteins essential for the vitality of the organisms.

W. D. H.

**The Relations of the Phenols and their Derivatives to Proteins. Mechanism of Disinfection. III. The Chemical Action of *p*-Benzoquinone on Proteins.** EVELYN A. COOPER (*Biochem. J.*, 1913, 7, 186—196).—*p*-Benzoquinone gives a red colour

with various proteins and amino-acids (confirmatory of Würster and Jachborski); the proteins can be isolated in a coloured state from the solutions, but could not be decolorised. Their solubilities and other properties are changed, hence they had been chemically altered. *p*-benzoquinone in absolute alcohol does not produce the colour; and treatment of the proteins with formaldehyde inhibits the reaction, except in the case of gelatin, aniline, and ammonia. The effect of formaldehyde indicates that proteins, proteoses, and amino-acids react with *p*-benzoquinone through their amino- or imino-groups. No colour reaction was obtained with *p*-benzoquinonedioxime, which shows probably that the reacting groups of the proteins condense with the ketonic groups of the quinone. The effect of the latter therefore resembles that of formaldehyde. Acetone differs from *p*-benzoquinone by acting as a protein precipitant. The germicidal power of *p*-benzoquinone is due to its chemical action on some constituent protein or proteins of the bacteria. W. D. H.

**Nitro-derivatives of the Proteins.** ALBRECHT KOSSEL and FRANZ WEISS (*Zeitsch. physiol. Chem.*, 1913, 84, 1—10).—The arginine group in the molecule of the higher proteins is as accessible to nitration by means of a mixture of concentrated nitric and sulphuric acids as that in the protamines.

Nitroclupine, like nitroarginine, when digested at 35° with normal sodium hydroxide solution loses carbon dioxide, ammonia, and nitrous oxide, a derivative of ornithine being formed. The amount of gas formed confirms this interpretation of the change, and the method is applicable to the determination of the nitro-group in nitroguanidine and of the nitroamino-groups in nitrated proteins.

In the case of edestin it is shown that in addition to the guanidine complex of the arginine constituent a further guanidine complex is present in the molecule, which forms a nitroamine. This is in agreement with Otter's (A., 1904, i, 1067) suggestion of such a second guanidine complex in  $\psi$ -mucin, casein, and gelatin. E. F. A.

**Action of Arsenious Acid, Arsenic Acid, and Phosphoric Acid on Albumin.** CORRADO BONGIOVANNI (*Gazzetta*, 1913, 43, i, 161—163).—From measurements of the conductivity of solutions of albumin and of the above acids separately, and of the binary mixtures of the acids with albumin, the author finds no evidence that combination with the albumin occurs. The diminution of conductivity which takes place on mixing is to be ascribed to a lessening of the mobility of the ions by the colloidal substance. R. V. S.

**Acid Decomposition Products of Hæmin.** OSKAR PILOTY and ERMUND DORMANN (*Ber.*, 1913, 46, 1002—1008).—The acid decomposition products of hæmin obtained on reduction with hydrogen iodide and acetic acid contain four components: ponopyrrolecarboxylic acid, xanthopyrrolecarboxylic acid, isoponopyrrolecarboxylic acid, and an acid so far only obtained as a syrup.

In view of the possibility that xanthopyrrolecarboxylic acid,  $C_{11}H_9O_2N$ , might be isoponopyrrolecarboxylic acid,  $C_{11}H_{13}O_2N$ ,

contaminated with the product of the action of ethyl alcohol on its picrate, it has been further investigated and its individuality established.

The picrate of phonopyrrolecarboxylic acid when heated in ethyl or methyl alcoholic solution in presence of free picric acid is rapidly and completely esterified at the carboxyl group. The free methyl ester crystallises in long, flat, colourless needles, m. p.  $59^{\circ}$ ; its picrate  $m. p. 122^{\circ}$ . The corresponding ethyl ester forms six-sided, colourless plates, m. p.  $134^{\circ}$ ; its picrate crystallises in pale yellow, flat, prismatic needles of rhombic habit, m. p.  $93^{\circ}$ .

The acid mixture yields a fourth crystalline acid,  $C_{10}H_{13}O_4N$ , *phonopyrrolecarboxylic acid-d*, which crystallises in colourless needles pointed at either end. The picrate separates in characteristic yellow crystals, m. p.  $132^{\circ}$ . The new acid is perhaps identical with compounds described by H. Fischer (A., 1912, i, 384, 901), and obtained by the action of sodium methoxide on pyrrole derivatives. E. F. A.

**Sulphuric Acid Hæmatoporphyrin.** ANT. HANSIK (*Zeitsch. physiol. Chem.*, 1913, 84, 60—66).—Hæmatoporphyrin, prepared from hæmin by means of concentrated sulphuric acid, was obtained as an amorphous, dark blue powder. By solution in acetic acid containing 10% of water, the addition of concentrated hydrochloric acid, and enough dilute acid to make the amount of water 40%, the pigment was obtained partly crystalline in dark green needles or long rods, usually aggregated in stellate or bunched clusters, and partly crystalline in red aggregates of varying size, or in indefinite green masses.

Crystals were also obtained by dissolving the original product in acetone and hydrochloric acid. E. F. A.

**The Kinetics of Invertin Action.** LEONOR MICHAELIS and (Miss) MAUD L. MENTEN (*Biochem. Zeitsch.*, 1913, 49, 333—369).—The authors, whilst accepting generally Victor Henri's generalisations as to the method of the ferment action, call attention to two defects in his experimental method. They show that the hydrogen-ion concentration of the solutions has not been taken into account, and that the multi-rotation of sugar has been neglected. They remedy the first defect by working in an acetate mixture, prepared according to Sørensen, which gives the optimal conditions of action, and they remedy the second defect by reading the polarisations after the sugar mixture has been allowed to remain with sodium hydroxide solution, which inhibits the action of the ferment. Like Henri, therefore, they use the polarimetric method for investigating the change. They assume that the invertin enters into combination with sucrose to form a labile compound, which decomposes according to the scheme: 1 mol. sucrose-invertin compound  $\rightarrow$  1 mol. dextrose + 1 mol. levulose + 1 mol. invertin. It is only through the intermediation of the sucrose-invertin compound that inversion takes place. The invertin can also combine with the scission products to form compounds, but as these are not labile, the only effect of their formation is to diminish the amount of ferment available for combination with the sucrose, and thus to inhibit the inversion. The present communication deals chiefly with the

methods for the determination of the dissociation constants of the various invertin-sugar compounds. For sucrose, the following equation is evolved:  $v = C\Phi \cdot [S]^2 / ([S] + k)$ , where  $v$  is the initial reaction velocity,  $C$  is a constant depending on the arbitrarily chosen units employed for measuring change (in this case the rotation changes),  $S$  is the concentration of the sugar,  $k$  the dissociation constant, and  $\Phi$  the concentration of the ferment. If  $\Phi$  is kept constant and  $S$  is altered,  $v/C\Phi$  can be replaced by  $V$ , and the equation becomes  $V = [S] / ([S] + k)$ , which is identical in form with the residuary dissociation curve of an acid. The methods are given (graphic and others) for determining  $k$ , which for the sucrose-invertin compound was found to be 0.0167. By measuring the inhibition of inversion produced by various carbohydrates, the dissociation constant of the compounds of invertin with other sugars was ascertained. For this purpose the equation:  $k = Fk' / \{ (S + k)(v_0/v_1 - 1) \}$ , was evolved, where  $k'$  is the constant in question,  $F$  is the amount of inhibitory sugar,  $v_0$  and  $v_1$  the initial rates of inversion in the presence and absence of inhibitory sugars (such as levulose), and the other symbols have the meanings already described. It was found that mannitol and glycerol, as well as carbohydrates, had a power of combining with invertin, but that the affinity for these of the ferment, as determined by the dissociation constants, was less than that for sucrose. Lactose had practically no combining power, and therefore does not appreciably inhibit sugar inversion. The decomposition of the sucrose-invertin compound was found to be a unimolecular reaction.

S. B. S.

**The Dialysis of Maltase.** JADISLAS KOPACZEWSKI (*Compt. rend.*, 1913, 156, 918—921).—A sample of maltase (taka-diastase) was submitted, first to ordinary dialysis, and then to Dhérès process of electrical dialysis (compare A., 1910, ii, 515). Ordinary dialysis causes the hydrolysing power of the maltase to increase very considerably to a maximum (200% of original power), after which it diminishes slightly to 180%. Prolonged dialysis produces no further change. Electrical dialysis at this stage removes more of the electrolytes present, and produces a slight further diminution in the diastatic power. The maltase travels in the electrical field towards the negative pole: thus purified, the maltase has a feebly acid reaction to leucanthin, and conductivity measurements give  $K = 3.8 \times 10^{-6}$ .

W. G.

**Action of Ammonia Gas on Diastase.** III. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 84, 161—188. Compare A., 1912, i, 113).—When dry ammonia gas is passed over diastase preparations a small quantity is absorbed. In addition to ammonium salt formation and physical adsorption, ammonia is taken up and an equivalent of water liberated in two ways. In one instance an atomic group is formed, which combines both with acids and with formaldehyde; in another, the new group has neither of these properties. Such changes are assumed to indicate the replacement of an alcoholic hydroxyl by an amino-group and the interaction of an aldehyde group with ammonia.

The enzymic activity of the diastase is increased rather than hindered by the action of the ammonia. It is assumed that diastatic activity is not connected with the presence of a free aldehyde group or of an alcoholic hydroxyl. E. F. A.

**The Reversibility of Ferment Actions: Emulsin and  $\beta$ -Methyl Glucoside.** EMILE BOURQUELOT and EMILE VERDON (*Compt. rend.*, 1913, 156, 957—959).—Experiments on  $\beta$ -methyl glucoside and emulsin confirm in every respect the results previously obtained with  $\beta$ -ethyl glucoside (compare Bourquelot and Bridel, A., 1912, i, 928; this vol., i, 212; Bourquelot and Coirre, this vol., i, 410). W. G.

**Action of High Temperatures on the Dried Nucleases of Vegetable Origin.** E. C. TRODORESCO (*Compt. rend.*, 1913, 156, 1081—1084. Compare A., 1912, i, 1042).—A study of the effect of heat on the enzymatic properties of dried nucleases from four different sources of vegetable origin. The dried nucleases of the plants studied only lose their activity towards sodium nucleate after heating for thirty minutes at the following moderately high temperatures. The nuclease from *Exsernia pruvastri* becomes inactive at 145°, that from *Lycoperdon gemmatum* between 141° and 156°, that from brewer's yeast at 153°, and that from *Sticta pulmonacea* at 162°. W. G.

**Preparation of a Nitro-3-amino-phenyl-1-arsinic Acid.** FARBERWKE VORM. MEISTER, LUCIUS & BREXING (D.R.P. 256343).—Two isomeric nitro-aminophenylarsinic acids are known, and the third isomeride has now been prepared as follows:

*Carboethoxy-m-arsanilic acid*, m. p. 180° (decomp.), is obtained by treating an aqueous solution of 3-aminophenylarsinic acid with ethyl chloro-formate; this, when dissolved in fuming sulphuric acid at 0° and treated with nitric acid (26%), furnishes the corresponding nitro-compound (a yellow, crystalline powder), which, on hydrolysis at 70—80° with concentrated sulphuric acid, gives rise to 2-nitro-3-aminophenylarsinic acid, orange-yellow needles.

2:3-Diaminophenylarsinic acid, obtained by reducing the preceding compound with sodium hyposulphite at the ordinary temperature, forms glistening leaflets, m. p. 205—208°; it furnishes an azoimide on treatment with nitrous acid.

2-Nitro-3-hydroxyphenylarsinic acid is obtained by the action of concentrated potassium hydroxide on 2-nitro-3-aminophenylarsinic acid, and this on reduction with sodium hyposulphite gives rise to 2:2'-diamino-3:3'-dihydroxyarsenobenzene. F. M. G. M.

## Physiological Chemistry

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**Oxidising and Reducing Enzymes and their rôle in the Process of Respiration.** ALEXIS BACH (*Arch. Sci. phys. nat.*, 1913, **35**, 240—262).—A summary of the present knowledge of the subject. Emphasis is laid on the following conclusions: (1) In order to utilise the oxygen of the air to effect oxidation, the cell produces an enzyme (an oxygenase), a substance which is readily oxidised, fixing molecular oxygen to form a peroxide. (2) A second enzyme (the peroxydase) accelerates the oxidising action of the peroxides, acting on them in the same way as ferrous sulphate does towards hydrogen peroxide. (3) The peroxides are readily transformed by hydrolysis into hydrogen peroxide, which is also formed as a primary product during hydrolytic oxidation. Owing to its rapid rate of diffusion, this accumulation of hydrogen peroxide might damage the cell protoplasm. To guard against this, the cell produces an enzyme-catalase, which rapidly decomposes hydrogen peroxide into water and inert oxygen. Catalase thus acts as a regulator of the respiratory process. (4) To effect hydrolytic oxidation, an enzyme, perhydridase, is present, which accelerates both oxidation and reduction just as do the metals of the platinum group. The reductase consists of the enzyme, water, and an oxidisable substance which fixes the oxygen derived from the water, leaving the hydrogen free to effect reduction. E. F. A.

**Mechanism of Stimulation by Lack of Oxygen.** H. S. GASSER and ARTHUR S. LOEVENHART (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxx—xxxii; *J. Biol. Chem.*, **14**).—Lack of oxygen decreases the oxidation, and so stimulates the cells of the respiratory, cardio-inhibitory, and vaso-motor centres. Decrease in oxidation stimulates per se, and not by the accumulation of katabolic products.

W. D. H.

**The Relationship between the Sugar Content of Erythrocytes and Glycolysis.** ADAM LOEB (*Biochem. Zeitsch.*, 1913, **49**, 413—423).—Observations of previous observers are confirmed, according to which the red blood corpuscles of different species possess different contents of sugar, which are characteristic of each species. In the case of man, the corpuscles contain about the same percentage of sugar as the serum; in the dog they contain less, and in the case of sheep and pig, the corpuscles only contain very small amounts of sugar. The corpuscles of ox occupy an intermediary place as regards the sugar content. The larger the sugar content of corpuscles, the greater the amount of glycolysis they produce on incubation. The conclusion is drawn that those corpuscles produce glycolysis most readily which are the most readily permeable by sugar. Glycolysis of added sugar is therefore not wholly dependent on the presence of white corpuscles. S. B. S.

**Oxycholesterol.** E. SCHREIBER and LÉNÁRD (*Biochem. Zeitsch.*, 1913, **49**, 458—465).—This substance pre-exists as such in the blood. It is also found in the brain, lungs, heart, intestine, spleen, kidneys, muscles, sometimes in the pancreas. It is, however, not present in the liver. The failure to find the substance in this organ is shown not to be due to imperfect technique. Oxycholesterol is absent from the blood in diabetic coma. Preliminary experiments are described which are directed towards ascertaining the action of the liver towards oxycholesterol. S. B. S.

**The Nature of the Destruction of Hæmoglobin during the Autolysis of Organs.** SOICHIRO MIURA (*Biochem. Zeitsch.*, 1913, **49**, 137—143).—The disappearance of the blood pigment from autolysing mixtures, as observed by Hess and Saxl, is confirmed. This is not due to an enzyme in the mixture, but is a coagulative process, which takes place rapidly in the presence of chloroform, which is used as an antiseptic; the blood colour disappears from solution, in fact, when a solution is incubated with chloroform, without the presence of any organ. The hæmatin component remains unchanged in quantity during the process of incubation. When organs are present, the coagulum is carried down with the solids. S. B. S.

**The Action of Leucocytes on Some Hexoses and Pentoses.**  
**III. Mechanism of Lactic Acid Formation from Carbohydrates.** PHÉBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **14**, 149—154).—Leucocytes transform dextrose into *d*-lactic acid, but cleavage does not proceed further. There must be many intermediate stages in this change. Embden's view that glyceraldehyde is one is not confirmed. Moreover, regardless of the nature of the hexose (mannose, lavulose, galactose, dextrose), the lactic acid is invariably of the *d*-form. Whether pyruv aldehyde is the phase immediately preceding the formation of lactic acid remains to be established. Tissues preserved under aseptic conditions act similarly. Dissociation of pentoses by leucocytes does not occur. W. D. H.

**The Behaviour of Calcium in the Serum.** PETER RUNA and DENGŌ TAKAHASHI (*Biochem. Zeitsch.*, 1913, **49**, 370—380).—The dependence of the solubility of calcium on the hydrogen and hydrogen carbonate concentration was investigated. The values, according to the laws of mass action of  $k_1 = [\text{Ca}^{++}][\text{HCO}_2^-]/[\text{H}_2\text{CO}]$  and  $k_2 = [\text{Ca}^{++}][\text{HCO}_2^-]/[\text{H}]$ , were determined. The experimental method of determining these constants is given in detail, and the values  $k_1 = 116 \cdot 10^{-6}$  and  $k_2 = 350$  were found. Serum was submitted to dialysis against an outer fluid of definite volume of known hydrogen carbonate concentration, and the composition of the inner and outer fluids was ascertained when equilibrium had been established. From the data thus obtained, the conclusion is drawn that the calcium hydrogen carbonate is in free diffusible form, but forms metastable supersaturated solutions. By the method of con.

permeation dialysis, against known phosphate mixtures, results were obtained indicating that the phosphate is also freely diffusible. The non-diffusible calcium appears therefore to exist in the form of calcium protein compounds. S. B. S.

**Mode of Action of the Anti-coagulating Substance of the Plasma of Propeptone.** HENRI STASSANO (*Compt. rend.*, 1913, 156, 912-915).—A continuation of previous work (compare this vol., i, 418) on the coagulation of the plasma of propeptone. On diluting samples of the plasma with equal volumes of solutions of different chlorides of equivalent strength, the period of time, prior to coagulation, increases with rise in molecular weight of the chloride. Diminution of the saline concentration by dialysis, or marked increase of it by addition of sodium chloride, produces coagulation. Addition of a strongly negative colloid hastens coagulation. The following conclusions are drawn: (1) In the plasma of propeptone the coagulation, *in vitro*, takes place in two stages: activation of the fibrin-ferment, followed by its action on the fibrinogen. There is also a third stage, commencing when the colloidal stability of the fibrinogen is brought about, which consists in the appearance of granules in the uniform gel, this phenomenon being very fugitive and only visible under the ultramicroscope in the case of blood. (2) The anti-coagulating substance of the propeptone plasma forms a complex with the fibrinogen, hindering its precipitation and giving rise to a coagulum, without the intervention of one of the above-mentioned methods. W. G.

**Digestion in the Chick.** T. P. SUAW (*Amer. J. Physiol.*, 1913, 31, 139-446).—Extracts of the glandular structures of the floor of the mouth in the chick contain an amylolytic enzyme active in an alkaline medium. This was found in extracts made an hour after hatching. The crop secretes no enzymes, but simply retains the food whilst salivary digestion goes on. By the second day, the gastric juice secreted contains proteolytic and milk-curdling enzymes which are active in an acid medium. The functions of the pancreas are imperfectly developed before the seventh day after hatching; the pancreatic juice then contains the usual three eozymes. The liver contains glycogen on the twentieth day of incubation; it becomes glycogen-free twenty-four hours after hatching if no food is given. It is found in the liver on the second day after the administration of starchy food. Lactose is not a glycogen-former in chicks, but acts as an irritant to the gastric and intestinal mucous membrane. W. D. H.

**The Dependence of Lipase Action on the Concentration of the Hydrogen Ion.** HEINRICH DAVIDSON (*Biochem. Zeitsch.*, 1913, 49, 249-277).—The lipolytic action was investigated by the statimetric method with the employment of tributyrin as substrate. The optimal action of the duodenal lipase of sucklings (withdrawn by means of a tube) was at  $[\text{H}^+] = 3.2 \times 10^{-9}$  or  $p_{\text{H}} = 8.5$ . A series of experiments was carried out with the same amount of



ferment in solutions of different hydrogen ion concentrations, and the course of lipolysis investigated. It was assumed that, except under optimal conditions, a fraction only of the ferment was active, and a method is given of calculating this fraction. If this amount is plotted graphically as a function of the hydrogen ion concentration, a curve is obtained which is identical with the dissociation curve of a weak acid, and is of the same order of magnitude as a curve deduced in a similar manner for trypsin. The conclusion is drawn that the lipase, like trypsin, is an amphoteric electrolyte with the acid dissociation constant  $k_a = 1.0 \times 10^{-7}$ . The lipolytic activity is proportional to the amount of ferment ion present. The lipase of the stomach has a broad optimal zone with  $[H^+]$  between  $10^{-3}$  and  $10^{-4}$ . The curve obtained for this ferment is similar to the invertin curve, and is that of the residuary dissociation curve of an ampholyte with the constant  $k_a = 4.5 \times 10^{-7}$ . The active principle of the stomach lipase is bound to the dissociation residue, and the optimal activity corresponds with the isoelectric point of the ampholyte, the basic dissociation constant of which is about  $10^{-4}$ . There is therefore a difference between the gastric and duodenal lipases, which can be distinguished from one another by ascertaining the optimal  $[H^+]$  concentration for their action. There is no evidence in the case of sucklings of regurgitation from duodenum. The lipase of human milk is apparently a pancreatic lipase.

S. B. S.

**Method of Investigating Metabolism in Rabbits, Milk being the Only Food.** ERNST LAQUEUR (*Zeitsch. physiol. Chem.*, 1913, **84**, 109—116).—A specially constructed cage for metabolism experiments on rabbits is described. For prolonged periods milk was the only nutriment given. The advantages of milk are that its nitrogen is easily estimated, the urine does not readily decompose, and its secretion is regular. The absorption of milk is rapid, and 95% of it is utilised as compared with 65—70% of oats and cabbage.

W. D. H.

**Amino-acids and Sugar for Rectal Feeding** HUBERT W. BYWATERS and A. RENDLE SHORT (*Arch. exp. Path. Pharm.*, 1913, **71**, 426—445).—The older observations on the nutritive value of enemata are untrustworthy. Not a trace of milk or egg (peptonised for twenty to thirty minutes) is absorbed. Amino-acids, however, are absorbed, and lead to an increase in urinary nitrogen; the ammonia is low in the urine, hence the absorption of putrefaction products is absent. Dextrose is better absorbed than lactose; fat is badly absorbed. The best enema for rectal feeding is milk which has been subjected to pancreatic digestion for twenty-four hours plus 5% of dextrose.

W. D. H.

**The Functions of the Liver in the Metabolism of Fats** I. HENRY S. RAPER (*J. Biol. Chem.*, 1913, **14**, 117—134).—Cocaine oil given to cats or dogs by the mouth can be detected in the liver in five to six hours. The amount present does not exceed 6% of

that absorbed. If cocoanut oil soap plus glycerol and bile are injected into the intestine of anesthetised cats, about 30% of the absorbed fatty acid is found in the liver. If an emulsion of the oil is given intravenously, 25–60% is found in the liver. During absorption the fat in the chyle contains fatty acids with an average higher molecular weight than in the oil. The lower acids are therefore partly absorbed as sodium salts. The volatile acids from the liver absorb more iodine than those from normal livers. The increase is not great, but it probably indicates that saturated fatty acids containing 10, 12, or 14 carbon atoms may become unsaturated in the liver.

W. D. H.

**The Influence of Urea Administered by the Mouth on the Nitrogenous Metabolism of Pigs.** EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **84**, 218–222).—No evidence was found to support the view that urea in the food acts as a protein sparer. In reference to gelatin, attention is drawn to the fact that various commercial specimens yield as much as 1% of tyrosine, and may even yield tryptophan. It is evident that no certain conclusions as to the nutritive value of gelatin can be drawn from experiments with such variable material.

W. D. H.

**Nitrogen Retention after Feeding on Urea. Reply to Abderhalden and Lampé.** EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, **84**, 234–238).—Polemical. The author maintains the correctness of his earlier conclusions.

W. D. H.

**Influence of Caffeine on Creatine and Creatinine Metabolism.** WILLIAM SALANT and J. B. RIEGER (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxv; *J. Biol. Chem.*, **14**).—Caffeine causes a moderate increase in the urinary creatine in fed rabbits, but a large increase during inanition; in some experiments, however, neither creatine nor creatinine were affected. Experiments on dogs gave negative results.

W. D. H.

**Metabolism of Nitrogenous Sugar Derivatives.** JAMES ARTHUR HEWITT (*Biochem. J.*, 1913, **7**, 207–210).—Dextrose-*p*-phenetidine given by the mouth or by injection is not toxic in amounts up to 4 grams per kilo. of body weight. It produces no effect on nitrogenous metabolism, but a reducing substance appears in the urine. Some escapes oxidation in the body; *p*-phenetidine in amounts of 0.1 gram per kilo. of body weight is highly toxic.

W. D. H.

**The Action of Carbon Dioxide on Metabolism. Autolysis and Metabolism. VI.** ERNST LAQUEUR (*Zeitsch. physiol. Chem.*, 1913, **84**, 117–160).—The nitrogenous metabolism was investigated on rabbits during a milk diet and inanition. Carbon dioxide slows and deepens the breathing; little or no narcotic action was observed. Nitrogenous metabolism was unaffected by a carbon dioxide percentage up to 7%. At 10% the output of nitrogen was increased,

at 13% very markedly so. In half the experiments this was accompanied by retention of water. The high tension of the gas is regarded as the cause of the increased decomposition of tissue-protein, possibly because the activity of autolytic enzymes is heightened.

W. D. H.

**Synthetic Powers of Animal Cells. The Action of Sodium Nitrate on Nitrogenous Metabolism.** EMIL ABDERHALDEN and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1913, **84**, 189—206).—Nitrogen given in the form of sodium nitrate is excreted quantitatively in the urine; it takes no direct part in protein metabolism. In two cases, however, there was retention of nitrogen, which did not correspond with the nitrogen given in the form of sodium nitrate. This is important as showing that nitrogen retention may be the result of the administration of nitrogenous materials which do not participate in metabolism.

W. D. H.

**Utilisation of Ammonia Nitrogen in Protein Metabolism.** ALONZO E. TAYLOR and A. I. RINGER (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxvi—xxvii; *J. Biol. Chem.*, **14**).—The findings of Grafe and of Abderhalden are confirmed, that starving and diabetic animals may retain a considerable part of the nitrogen ingested as ammonium carbonate.

W. D. H.

**Nitrogenous Assimilation on Feeding on Small Amounts of Protein and Large Amounts of Ammonium Salts and Urea.** EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, **84**, 69—96).—The favourable action of ammonium salts and urea given by the mouth in pigs in causing retention of nitrogen is supported by further experimental data. By themselves, however, they do not maintain nitrogenous equilibrium over prolonged periods, but in combination with a small amount of protein they do. In other words, they have a protein sparing action. Whether their nitrogen is converted into protein or not is discussed, but no definite conclusion reached. The paper concludes with polemics against Abderhalden and Lampé, whose experiments are held to support and not disprove the author's contentions.

W. D. H.

**The Location of Protein Synthesis and the Production of Nitrogenous Equilibrium with Minimal Amounts of Proteins of Varying Decomposibilities.** HANS STECK (*Biochem. Zeitsch.*, 1913, **49**, 195—224).—It has been assumed that the chief seat of synthesis of proteins is in the mucous membrane of the small intestine. If this is the case, those proteins which most readily undergo enzymatic hydrolysis into their constituent amino-acids will be the most efficient in maintaining nitrogenous equilibrium (that is, will maintain equilibrium when ingested in the smallest quantity), provided that the energy needs of the organism are sufficiently satisfied by the caloric value of the fats and carbohydrates. The reason for this assumption is that the majority of the amino-acids necessary for protein synthesis will be present at

the same time in the intestine in those proteins which are readily hydrolysed. The method of experiment adopted by the author was to place himself on a diet of sufficient caloric value and nearly free from nitrogen, and then to estimate the nitrogen loss. On this diet various proteins were superimposed, and the quantity was ascertained in each case, which is just necessary to restore the nitrogenous equilibrium. It was found that after three days of protein-free diet, the superimposition of small quantities of beef, egg-albumin, and caseinogen could restore equilibrium, but the amounts bore no relationship to their decomposability by proteoclastic ferments. The conclusion is drawn therefore, that protein synthesis takes place in parts of the organism other than the small intestine. From the amounts of nitrogen secreted in the after period, it appears that the ingestion of these proteins results in protein synthesis in the organism. Hæmoglobin, when ingested in small quantities, was inefficient in maintaining nitrogenous equilibrium. S. B. S.

**The Influence of the Plane of the Protein Intake on Nitrogen Retention in the Pig.** ELMER V. MCCOLLUM (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxxiii—xxxiv; *J. Biol. Chem.*, 14).—The retention of nitrogen at all levels, except 7.5 times the endogenous level, was in close agreement, whether the proteins given were derived from wheat, oats, or maize. At five times this level, 10% of the ingested nitrogen was retained; at 7.5, 12—17%; at 10, 15, and 20, the retention was 21—24%. W. D. H.

**Metabolic End-Products of the Lipoid Nitrogen of Egg-yolk.** ELMER V. MCCOLLUM and H. STEENBOCK (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xlv—xlv; *J. Biol. Chem.*, 14).—A pig was fed for a week on 220 grams of dry egg-yolk and 35 grams of starch per diem. The nitrogen intake was 11.65 grams daily; of this, 0.65 gram was lipoid nitrogen. The urinary nitrogen varied from 5 to 8 grams; of this 30 to 40% was in the form of ammonia, and only 35—45% as urea. The urine contained 0.3 gram of nitrogen as substituted amines. The demethylation of substituted amines is evidently not readily accomplished in the pig's body. W. D. H.

**The Biological Value of  $\alpha$ -Nucleic Acid.** G. ALLESANDRO BROSSA (*Chem. Zentr.*, 1912, ii, 2123; from *Arch. Anat. Physiol. Physiol. Abt.*, 1912, 191—196).—A dog and two hens were reduced to a nitrogen-free diet balanced by increased amounts of carbohydrates and fats, and then supplied with  $\alpha$ -nucleic acid. Estimation of nitrogen in the excreted substances showed that 60—80% of the nucleic acid, a compound which is far removed from the proteins, had been absorbed. J. C. W.

**Resorption of Bromide from the Intestine.** STEFAN VON BOGDANOV (*Zeitsch. physiol. Chem.*, 1913, 84, 15—17).—To study the resorption of bromide from the intestine, the blood stream was isolated to the intestine, heart, and lungs, and the haloids in it determined before and after injection of sodium bromide. The

bromide is shown to aggregate in the blood in a very short interval; part of the sodium chloride of the blood is replaced by bromide.

E. F. A.

**The Fate of Protein Cleavage Products in the Intestine.** EMIL ABDERHALDEN, ARNO ED. LAMPÉ, and EFIM S. LONDON (*Zeitsch. physiol. Chem.*, 1913, 84, 213-217).—Accepting the view that in absorption protein cleavage products enter the blood stream as amino-acids and ammonia, there still remains the possibility that the lacteals may be a channel for protein absorption. In two series of experiments on dogs, the lymph during digestion of meat was found to contain more nitrogen but less amino-acid than during hunger; the amount of ammonia was but little altered. Further work in this direction is promised.

W. D. H.

**The Absorption of Magnesium Sulphate Solutions in the Small Intestine, and the Mode of Action of Saline Purgatives.** RUDOLF COBET (*Pflüger's Archiv*, 1913, 150, 325-360).—The relative importance of physical and physiological factors in the causation of purgation by salines is discussed. Magnesium sulphate causes a great increase of secretion in the intestines; the sodium chloride of the intestinal juice poured out is re-absorbed in the lower reaches of the gut, but the fluid portion is not; the sulphate itself is badly absorbed.

W. D. H.

**Intestinal Obstruction. A Toxic Substance in the Intestinal Mucosa.** GEORGE H. WHIPPLE (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxxii-xxxiii; *J. Biol. Chem.*, 14).—Closed loops of the small intestine yield what normal mucosa does not yield, a toxic substance which causes low blood-pressure, vomiting, diarrhoea, collapse, and death. If the mucosa is first destroyed by sodium fluoride, no toxic substance is formed.

W. D. H.

**The Influence of Function on the Lime Requirements of Animals.** H. STEENBOCK and EDWIN B. HART (*J. Biol. Chem.*, 1913, 14, 59-73).—In the non-pregnant animal a daily intake of 0.3 gram of CaO in the pig, and 0.4 in the goat per 100 lbs. of body-weight covers metabolic losses; but mammary activity is a severe drain on the skeletal lime, and the allowance in the food should be three or, better, six times greater, for increase of food entails large losses of lime in the intestine.

W. D. H.

**The Effect of a High Magnesium Intake on Calcium Retention in Swine.** EDWIN B. HART and H. STEENBOCK (*J. Biol. Chem.*, 1913, 14, 75-80).—Bran is not a good bone-producer, on account of its low lime content. Magnesium salts added to a pigs' ration increase the urinary calcium, but this is counteracted by di-potassium hydrogen phosphate. The inter-relations existing between the mineral elements are important factors in nutrition.

W. D. H.

The Behaviour of Plasteins in the Animal Body. ERICH VON KNAFFL-LENZ and ERNST P. PICK (*Arch. exp. Path. Pharm.*, 1913, 71, 407-425).—Plasteins act as antigens, but the immune material generated is not specific. The specificity of the original proteins is thus destroyed during digestion. It further makes no difference what variety of pepsin is employed in their formation. Plasteins do not produce the phenomena of anaphylaxis.

W. D. H.

The Influence of the Composition and Amount of the Mineral Content of the Ration on Growth. ELMER V. McCULLUM and MARGUERITE DAVIS (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xl; *J. Biol. Chem.*, 14).—Young rats do not grow when fed on wheat kernel only, but the addition of salts so as to make the ration like that of milk or egg-yolk produced normal growth.

W. D. H.

The Chemical Changes Occurring in Meats during Drying in Vacuum. L. H. DAVIS and A. D. EMMETT (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xlii; *J. Biol. Chem.*, 14).—Calculating the data for fresh and desiccated meats to the dry basis, using the two values for dry substance (the vacuum and the oven-heated), the results agree closely for the various constituents, the differences being greatest in the fat, as was to be expected.

W. D. H.

The Presence of Choline or Allied Bases in the Saliva of the Horse. JULES HODAS (*Compt. rend.*, 1913, 156, 824-826).—Schulze and Trier (*A.*, 1912, ii, 1203) having demonstrated the presence of choline and allied bases in all plants, the author has examined the saliva of horses for the presence of these substances therein, using Bouchardat's reagent to recognise them. Specimens of saliva were obtained from horses under varying conditions and at different times after feeding and with varying diet, and in all cases either choline or bases of the same group were found to be present.

W. G.

The Central Nervous System under Normal and Pathological Conditions. V. Biochemical Studies on Brain Swelling; (a) Acute Brain Swelling and the Colloidal Theory of Oedema. GIACOMO PICHINI, PIETRO BARBIERI and DOMENICO CARBONE (*Biochem. Zeitsch.*, 1913, 49, 293-316).—According to the theory of M. Fischer, oedema is due essentially to inhibition of water, which, in the case of proteins, takes place more readily in the presence of alkalis and bases, and is inhibited by salts. The authors discuss the subject of brain swelling from the clinical and pathological point of view, and suggest as a possible cause for the inhibition of water by the brain an increase of acid in the circulation. They have, however, failed to substantiate the hypothesis, as the injection of acids under varying conditions into animals (rabbits) did not produce oedema.

S. B. S.

**The Fatty Acids of the Human Brain.** EGERTON CHARLES GREY (*Biochem. J.*, 1913, 7, 148—156).—At least 25% of the solid fatty acids of the brain are hydroxy-acids; of these, three have been isolated:  $C_{17}H_{33}O_3$  or  $C_{22}H_{41}O_4$ , m. p. 100—101°;  $C_{25}H_{51}O_3$ , m. p. 91·0°; and  $C_{29}H_{59}O_3$ , m. p. 73·5°, and two at least are mono-hydroxy-acids, and therefore are not produced artificially by oxidation of unsaturated fatty acids. The unsaturated acids include oleic, linoleic, and linolenic acids; also an acid still more unsaturated, to which the name *clupanodonic acid* is given; it combines with 12 atoms of bromine. Another is a solid,  $C_{18}H_{34}O_3$  or  $C_{18}H_{36}O_3$ , m. p. 42°; this is probably an isomeride of oleic acid. The saturated acids are stearic, palmitic, myristic, and Thudichum's neurostearic acid, m. p. 51—52°. The resemblance between the hydroxy-acids of the brain and those of lanoline is additional evidence of the relationship of nervous tissues to other tissues of epiblastic origin.

W. D. H.

**Action of Various Influences on the Mammalian Heart.** V. H. K. MOORHOUSE (*Amer. J. Physiol.*, 1913, 31, 421—438).—Isolated strips of the cat's auricle beat spontaneously in a bath of oxygenated Ringer's solution; the rhythm and effect of temperature are approximately equal in coronary, nodal, and septal strips. Drugs which act on the vagus are more effective on strips which do not contain nodal muscle. Drugs which act on sympathetic nerve-endings produce an equal effect on all these kinds of strip, but the acceleration lasts longest in septal strips. The sino-auricular node does not exhibit any specially reactive properties to various influences affecting rhythm.

W. D. H.

**The Action of Oxalic Acid on the Frog's Heart.** OSKAR GROS (*Arch. exp. Path. Pharm.*, 1913, 71, 395—406).—A solution of sodium oxalate added to Ringer's solution soon stops the heart of the frog in diastole. Its activity is restored by washing out with a calcium-free solution. Sodium citrate acts more powerfully in the same way, although its power to precipitate calcium is less. It is held that the removal of the calcium is not the cause of the action, but that oxalates and citrates have a specific harmful effect on cardiac tissue.

W. D. H.

**Diastases. II. Sugar Formation in the Frog's Liver.** I IVAR BANG (*Biochem. Zeitsch.*, 1913, 49, 40—86).—The experiments were carried out with both *Rana esculenta* and *R. fusca*. Sugar was estimated in separate lobes of the liver. As a rule, one lobe was separated from the others, and the sugar was estimated immediately, whilst the other lobes were allowed to remain in Ringer's fluid and the sugar was estimated after several hours. The amounts of sugar free and existing in the separate lobes from the same animal were also ascertained, and the limits of variation determined. From the alterations in weight after keeping in Ringer's solution, which were found to be small, the conclusion was drawn that the liver still survives even after prolonged keeping in the Ringer's

fluid, it being assumed that the organ is not killed, whilst its osmotic properties remain intact. Other reasons are also given for assuming that the organ survives after prolonged immersion in Ringer's solution. After keeping in this liquid, the livers show an increase of reducing sugar (found both in the organ itself and in the fluid in which it is immersed), the amount of which is larger than the variations in the lobes from the same animal. The conclusion was therefore drawn that the surviving liver is capable of producing sugars. The mechanism of this sugar production was studied. It is not due to the diastase of the blood, as there is no appreciable difference between the amounts produced in a liver containing blood and one that has been perfused (from the portal vein). There is, however, a considerable difference between the sugar production by the crushed liver paste and by the intact cells, according to whether the organs have been perfused or not. If they have not been perfused, the paste produces much more sugar, owing to the fact that the diastase of the blood can then act; where they have been perfused, the difference between the sugar production by the paste and intact cells is very much diminished. This is additional evidence of the fact that the sugar production by the surviving liver is not due essentially to the diastase of the blood. The facts indicate that it is due to a liver enzyme. In the case of *Rana esculenta*, the treatment of the liver with alcohol reduces the sugar-producing power of the liver, which can, however, be restored by addition of sodium chloride; in fact, when the liver has been treated in this way, the sugar-producing power is increased beyond that of the original intact liver. This fact is explained by the hypothesis that the alcohol removes some lipoid-like substance which exerts an inhibitory action on the sugar-producing power. As the addition of the alcoholic extract does not inhibit this power exerted by the extracted liver and salt, it is assumed that the inhibitory substances only exert their action when in some form of combination, which is broken up on treatment with alcohol, but not restored on the addition of the alcoholic extract. The same phenomena were not observed in the livers of *R. fusca*, which, unlike those of *R. esculenta*, do not appear to contain a large store of enzyme or pro-enzyme, which can be activated by the addition of salt.

S. B. S.

### Diastases. III. Sugar Formation in the Frog's Liver.

II. IVAR BANG (*Biochem. Zeitsch.*, 1913, 49, 81—119).—Adrenaline increases the sugar-producing power of the liver, in quantities which are insufficient to kill the organ. Details are given of Overton's experiments on the irritability of muscles after treatment with adrenaline which justify the conclusion as to the relative non-toxicity of the adrenaline solutions employed. A detailed account is given of the action of adrenaline on the sugar production of the liver under varied conditions. In the case of *R. fusca*, the increased production appears to be due to the reduction of the acidity of the medium, and the effect can be imitated by the use of neutral phosphate solutions. Furthermore, the accelerating effect of the adrena-



line in these cases can be antagonised by the presence of minute amounts of free hydrochloric acid. In the case of *R. esculenta*, the action of adrenaline appears to be exerted on the intracellular lipoids, which in combination inhibit the diastatic action of the organ (compare preceding abstract). The adrenaline action in this case can be imitated by treating the liver with narcotics (for example, alcohol), which can also break down the lipid complex. There is no evidence that adrenaline causes new production of enzyme; it appears only to activate the pre-existing ferment.

S. B. S.

**The Formation of Glycogen from Glyceraldehyde in the Liver.** JAKOB PARNAS (*Zentr. Physiol.*, 1912, 26, 671—672).—Perfusion of the tortoise's liver with glyceraldehyde in Ringer's solution leads to the deposition of glycogen therein, at the rate of about 50 mg. reckoned as dextrose per hour per 10 grams of liver. Whether this is due to condensation, or oxidation through the stages of glyceric acid, glycolaldehydecaboxylic acid, and glycolaldehyde is uncertain; the view that dextrose is katabolised into glyceraldehyde in the body is also unsettled.

W. D. H.

**The Importance of Cholesterol in the Organism.** LEON HAHN WACKER and WERNER HUECK (*Arch. exp. Path. Pharm.*, 1913, 71, 373—391).—The methods of estimation of cholesterol are discussed, but the microscopic examination of the adrenal cortex gives a good indication of the amount present. In this situation free cholesterol is an integral and stable cell constituent, but the cholesterol in the condition of ester is variable and labile. It is here that the polarising microscope is especially useful. In arterial sclerosis, chronic kidney disease, diabetes, and during pregnancy the amount of cholesterol esters increases, but in long-continued infectious disease, septic processes, chronic ulcer, cancer, and tubercle it falls. In the acute stages of infectious diseases, it increases. The amount in the blood varies directly as that in the suprarenal; this is regarded as important, for cholesterol plays a rôle in the natural protective processes of the body.

W. D. H.

**The Iodine-containing Complex of Thyroglobulin.** PAUL C. KOCI (*J. Biol. Chem.*, 1913, 14, 101—116).—The full activity of thyroid tissue (measured by Hunt's method) is contained in the thyro-globulin fraction. The full activity per iodine unit is still present in the metaprotein fraction from this globulin, although the iodine in this fraction is increased three-fold. Other products of hydrolysis (proteoses and iodothyron) show a decrease in activity per unit of iodine. The amino-acid fractions contain very little iodine, and are either inactive or nearly so. Tetra-iodohistidine anhydride and iodo-tryptophan have no activity.

W. D. H.

**Some Phosphatides of Human Placenta.** I. and II. C. SAKAKI (*Biochem. Zeitsch.*, 1913, 49, 317—325, 326—332).—The placenta was extracted with alcohol at 60°. A white substance

only sparingly soluble in cold alcohol was isolated, which was very similar in properties to the diaminophosphatide isolated by Thierfelder and Stern from egg-yolk. Its composition was intermediate between that of apomyelin and sphingomyelin, as isolated by Thudichum. A preliminary account of other products is given. No evidence as to the existence of jecorin was obtained.

In the second paper, a preliminary account is given of various fractions, none of which can be claimed to be a pure product.

S. B. S.

**Muscular Contraction; Influence of Non-electrolytes, Electrolytes, and Osmotic Pressure.** GEORGES KLEEFELD (*Bull. Acad. roy. Belg.*, 1913, 91—180).—The principal views of J. Loeb on the antagonism between calcium ions and those of potassium and sodium, as well as on the toxicity of sodium ions, are confirmed; perfusion with calcium chloride extinguishes muscular excitability; sodium nitrate has the same effect, and potassium is sometimes indifferent; at other times it abolishes excitability. Certain non-electrolytes (sucrose, dextrose) are capable of determining rhythmic contractions. Calcium is sometimes an excitant of contractility, and is able to render contractile muscles treated with sodium citrate. Calcium can exist in the perfusion fluids far above the normal amount without suppressing excitability. By the method of Lapicque-Weiss it can be shown, however, that electrical irritability can diminish, even although the muscle executes normal contractions. Contractility and irritability cannot be regarded as identical.

W. D. H.

**Amount of Creatine in Muscles of Various Animals and in Different Types of Muscles.** MARIO CARELLA (*Zeitsch. physiol. Chem.*, 1913, 84, 29—38).—Creatine is always present in the muscle tissue of vertebrates. The amount varies with the nature of the muscle; it is most in striped voluntary muscle, less in heart muscle, and least in unstriped muscle. In birds (hens, ducks) the amount of creatine in the breast muscles is considerably larger than that in the limb muscles.

Similar differences in the amount of creatine are found in the individual muscles of any one animal. These differences persist whether referred to the weight of fresh muscle or dried muscle, or expressed as creatine nitrogen in terms of the total nitrogen. This nitrogen factor lies between 3 and 4 for the voluntary muscles of mammals, birds, fishes, and the heart muscle of the ox. It is from 4 to 5 for the breast muscle of birds, and about 1 for the heart muscle of the hen and the smooth muscle of the ox.

Creatine could not be obtained from the muscular tissue of the mantle or the arms of the octopus.

E. F. A.

**Muscle-Creatine. Dialysis of Creatine from Dog's Muscle** R. T. LEO and PAUL E. HOWE (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xliii; *J. Biol. Chem.*, 14).—Creatine dialyses out from muscle into water, Ringer's solution, and various strengths of sodium chloride

solution. Hydrochloric acid delayed the diffusion, alcohol increased it. The experiments offer no definite evidence as to the way in which creatine is held in the muscle.

W. D. H.

**The Action of Potassium Chloride on Frog's Muscle.** RICHARD SIEBECK (*Pflüger's Archiv*, 1913, 150, 316—324).—Neutral isotonic solutions of potassium chloride render muscles rapidly inexcitable; the muscles increase in weight. Even after some hours, when there is a 20% increase in weight, the action is completely reversible. Organs the structure of which is destroyed by freezing and thawing, do not swell in solutions of potassium chloride, but swell in alkaline solutions. An acid reaction causes in muscle either in Ringer's or a potassium chloride solution no marked reversible effect; but the swelling is increased by faradic stimulation, an alkaline reaction, or by narcosis.

W. D. H.

**Connective Tissues of Limulus.** HAROLD C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xl—xli; *J. Biol. Chem.*, 14).—The cartilage-like tissue yields a sclero-protein which is insoluble in water and the ordinary solvents. It is insoluble in pepsin hydrochloric acid, but digests readily in a tryptic mixture. It gives the usual protein reactions, but no gelatin was obtained. The white, fibrous tissue within the carapace is also composed of a non-collagenous sclero-protein. It digests readily in a peptic, but very slowly in a tryptic, mixture.

W. D. H.

**The Secretion of Pigments by Annelids.** K. KSCHISCHKOWSKI (*Chem. Zentr.*, 1913, i, 40; from *Zentr. Physiol.*, 1912, 26, 528—532).—Under certain conditions, *Lumbriconereis impatiens* secretes a lilac-red pigment, which gives an orange solution in ether and a pink in chloroform. The secretion is provoked in a specific way by solutions of potassium salts which are isotonic with a 3.6% solution of sodium chloride. If the organisms are narcotised or kept in isotonic solutions free from potassium salts for some time, the pigment reaction does not occur for several days.

J. C. W.

**The Role of Glycogen, Lecithides, and Fate in the Reproductive Organs of Echinoderme.** BENJAMIN MOORE, EDWARD WHITLEY, and ALFRED ADAMS (*Biochem. J.*, 1913, 7, 127—141).—The male and female reproductive glands in echinoderms contain large amounts of reserve metabolic products, such as glycogen, fat, and lecithides. These reserves are only slowly used up, if at all, when the animal is deprived of food. In such glands no sugar formation occurs in a period of two days after death. The fatty substances are highly unsaturated, thus resembling liver oils.

W. D. H.

**The Basic and Acidic Proteins of the Sperm of Echinus esculentus. Direct Measurements of the Osmotic Pressure of a Protamine or Histone.** BENJAMIN MOORE, EDWARD WHITLEY, and ARTHUR WEBSTER (*Biochem. J.*, 1913, 7, 142—147).—A substance

was separated from the ripe male gonads of *Echinus esculentus*, which had properties intermediate between those of a histamine and a histone. Its molecular weight calculated from its osmotic pressure is 8780. Its action on ova and cell division was tested, but the results were negative.

W. D. H.

**Anoxybiose and Chemical Polarity.** (Mme.) ANNA DRZEWINA and GEORGES BOHN (*Compt. rend.*, 1913, 156, 810—812).—*Prostheceraeus* and *Convoluta* when placed in tubes deprived of oxygen for six hours and then returned to aerated water, in all cases exhibit the phenomenon that the anterior extremity has possessed a greater resistance to the privation of oxygen than the posterior extremity, the latter becoming disintegrated when returned to water, whilst the heads live and can be seen swimming about. This differentiation the authors compare with chemical polarity.

W. G.

**The Composition of Human Bile.** ERNST VON CZYHLARZ, ADOLF FUCHS, and OTTO VON FÜRTH (*Biochem. Zeitsch.*, 1913, 49, 120—129).—Details are given for the estimation of the following constituents of the bile: Total solids, pigment (colorimetric method), cholesterol (colorimetric method with chloroform and acetic anhydride), higher fatty acids, mucin, bile acids (as cholic acid). Typical analyses are given of bile obtained from the bladder and from fistulae. Administration of cholesterol *per os* appeared to increase, not the amount of cholesterol, but that of the bile acids in the bile obtained from a fistula.

S. B. S.

**Secretin and Vaso-dilatin.** L. LAUNOV and KARL OECHELIN (*Compt. rend.*, 1913, 156, 962—965).—By repeated precipitation by absolute alcohol from aqueous solution the authors have obtained the secretin of Bayliss and Starling (*A.*, 1902, ii, 275, 613; 1903, ii, 316) in a solid state as a non-hygroscopic, white powder, very soluble in water, having an alkaline reaction and a very marked exciting influence on the secretion of pancreatic juice, but no depressing effect. Further, on concentrating the alcohol used for the above precipitation, they obtained a yellow, hygroscopic powder, soluble in water, and having a strongly alkaline reaction. Its aqueous solution only produces feeble secretion excitation, but is strongly depressant. It corresponds with the "depressor substance" mentioned by Bayliss and Starling (*loc. cit.*). This shows that Popielski's vaso-dilatin (compare *A.*, 1912, ii, 593) is distinct from the above secretin.

W. G.

**An Attempt to Estimate the Vitamine-fraction in Milk.** CASIMIR FUNK (*Biochem. J.*, 1913, 7, 211—213).—In milk freed from protein the vitamine fraction is precipitable by phosphotungstic acid; the amount of vitamine ( $C_{12}H_{20}O_5N_2$ ) is about 1 to 2.5 mg. per litre. The filtrate still contains nitrogen, which probably represents allantoin. If milk is freed from fat by the centrifuge, about half the vitamine and allantoin is lost. Both allantoin and vitamine are destroyed by boiling.

W. D. H.

**The Secretion of the Two Kidneys.** RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, 156, 754—756).—An examination of the amount of urine flowing from each of the kidneys of a healthy dog and a determination of the urea, sugar, and chlorides present in each case. In every case there was a greater flow from the right side, and the urine from this side was richer in chlorides and sugar. The nitrogen-urea coefficient was the same for both sides. These differences are stated to be due partly to a difference in the secretion activity, but principally to differences in resorption of the urinary constituents by the two kidneys.

W. G.

**The Extremes of Variation of the Concentration of Hydrogen Ions in Human Urine.** LAWRENCE J. HENDERSON and WALTER W. PALMER (*J. Biol. Chem.*, 1913, 14, 81—85).—After a dose of 10 grams of monosodium phosphate there is a slight increase of hydrogen ion concentration in the urine. Larger quantities of acid phosphate or of hydrochloric acid produce a similar effect, but the acidity is never as great as in many pathological conditions. A more alkaline urine is produced by sodium hydrogen carbonate, but beyond a certain point even after large doses of alkali the reaction of the urine does not change. In a large number of observations the highest acidity exceeded 4.70; the highest alkalinity 8.70. This corresponds with a range of 1:10,000 in the concentration of hydrogen and hydroxyl ions. The actual variation in normal people is at least 0.5 gram-molecule. In pathological states the variation is greater. In most acid urines, the urinary acids are in large measure free; in most alkaline urines they are almost completely combined with bases.

W. D. H.

**Diastase in the Urine of Infants.** ERNST MAYER (*Biochem. Zeitsch.*, 1913, 49, 165—167).—Diastase is seldom completely absent from the urine of breast-fed children. In the first three months, however, it does not exceed 5 units (in Wohlgemuth's system). There is no appreciable increase in the next three months. Between the sixth and ninth month the values vary between 2.5 and more than 20 units, after which period higher values are obtained. The amount is, however, affected by pathological complications.

S. B. S.

**Excretion of Purine Katabolites in Sundry Types of Mammalia.** MAURICE H. GIVENS and ANDREW HUNTER (*Proc. Amer. Soc. Biol. Chem.*, 1912—13, xxiv—xxv; *J. Biol. Chem.*, 14).—Allantoin is a regular constituent of the urine of rabbit, horse, pig, cow, cat, dog, coyote, monkey, and man. To this list may be added the opossum, guinea-pig, porcupine, sheep, and racoon. In man the figure is smallest. Uricolytic power is greatest in carnivora; then follow rodents, ungulates, and marsupials in the order named. It is practically absent in man.

W. D. H.

**Estimation of Amylolytic Ferments in the Urine as a Measure of Certain Pathological Conditions.** DUDLEY CORBETT (*Quart. J. Med.*, 1913, 6, 351—383).—The amount of ferment passed

by a given individual in twenty-four hours' urine is fairly constant, varying between 6.6 and 33 Wohlgemuth units, the average being 10-20°. It is also present in blood serum, the average amount being 10 units. The quantity in the urine is unaffected by the diet, the reaction of the urine, the presence of bacteria, and other abnormal constituents, with the exception of blood. The amount in the urine does not appreciably diminish if the urine is kept in the presence of toluene. The amount in the urine of an infant fed on milk is very small, but rises on the administration of starchy food. When the amount of ferment in the serum exceeds that of the urine, there is a renal deficiency, as the ferment is readily excreted by normal kidneys. High readings were never obtained in pure cases of renal disease. High readings (up to 100 or even more) were found in certain acute infective conditions, in pancreatic disease, in certain forms of eclampsia, and in one case of "acidosis" in a child. All cases of undoubted pancreatic disease, whether due to malignant or inflammatory processes, gave high readings, and the test may therefore be of value for diagnosis of such conditions. In diabetics on strict diet, the readings were generally subnormal. In severe cases the readings were lower than in the milder forms, but in these conditions the excessive amount of urine excreted must be taken into account.

S. B. S.

**Sarcocollactic Acid and the Theory of Diabetes.** R. T. WOODYATT (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxxviii; *J. Biol. Chem.*, 14).—A theory is proposed that the internal secretion of the pancreas dissociates dextrose and perhaps other hexoses, and that the presence of lactic acid is evidence of such dissociation. In pancreatic diabetes there is lessened dissociation and less lactic acid in the tissues.

W. D. H.

**The Behaviour of Blood Sugar in Normal and Pathological Cases. VII. The Blood Sugar in Diabetes Mellitus.** FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, 49, 278-292. Compare this vol., i. 425).—No direct relationship was found between the amount of blood-sugar and glycosuria in diabetes. It was found that only in the case of severe diabetes did ingestion of proteins cause a rise both of blood-sugar and glycosuria. The blood sugar content did not increase either in the case of carnivora (dogs) or herbivora after administration of proteins. The administration of meat and carbohydrate foods caused a greater amount of glycosuria in diabetics than a similar diet in which the meat was replaced by vegetable proteins.

S. B. S.

**Sulphur Metabolism. I. The Urinary Sulphur Partition in Various Diseases.** N. STADTMÜLLER, MAX KAHN, and JACOB ROSENBLUM (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xlv; *J. Biol. Chem.*, 14).—High proportions of neutral sulphur were passed in nearly all cases of diabetes, in all cases of cancer, in one case of nephritis (out of two), and in the one case examined of hypopituitarism.

W. D. H.

**The Intestinal Flora. The Possible Production of Pto-  
maines in Acid Medium.** ALBERT BERTHELOT and D. M.  
BERTRAND (*Compt. rend.*, 1913, 156, 1027—1030. Compare A., 1912,  
ii, 668).—*Bacillus aminophilus intestinalis*, sown on media contain-  
ing histidine and peptone, to which were added, instead of dextrose,  
amounts of lactic acid varying from 0.5 to 5 per 1000, shows marked  
culture and formation of 4-β-aminoethylglyoxaline, even with 3 per  
1000 of acid present. Thus, in the intestinal flora of persons  
exhibiting, at the same time, symptoms of enteritis and colitis, their  
faeces being acid, the *B. aminophilus* may be found capable of  
attacking histidine even in a slightly acid medium. This bacterium  
is capable of acting in the intestine as a simple lactic ferment  
without forming any toxic base, but it can, in certain cases, produce  
aminoethylglyoxaline equally well in neutral or alkaline medium,  
or in the presence of acids elaborated by other microbes, and its  
attack is not limited solely to histidine. W. G.

**The Action of Aloin on Metabolism. The Physiology of  
Artificially Produced Gout and Fever.** M. BERRAR (*Biochem.  
Zeitsch.*, 1913, 49, 426—446).—It has already been shown by Kossel,  
that administration of aloin to birds produces increased output of  
uric acid, which, in cases where the action of the kidneys is  
inefficient, leads to the production of an artificial gout. The  
researches on aloin have now been extended to mammals. Quantities  
of 0.1 to 0.2 gram per kilo. of body weight, administered to dogs,  
produces an increase of temperature and increased metabolism,  
which at the height of action can be double the normal. Both the  
gaseous metabolism and the output of various products in the urine  
and faeces were investigated. The substances forming the source  
of the increased energy production were those most readily at the  
disposition of the organism at the time of the administration of  
the drug. In the starving animal, the fat and proteins served  
chiefly for this purpose, whereas in the case of an animal which  
had received a diet rich in carbohydrates, these substances were  
mostly drawn upon, their metabolism increasing from 150 to 500%,  
the normal value. No distinct relationship was ascertained between  
the amounts of different products employed to meet the increased  
energy needs. S. B. S.

**Use of the Oxydase Reaction in the Differentiation of  
Acute Leucæmias.** JOHN SNOW DUNN (*Quart. J. Med.*, 1913, 6,  
293—308).—The occurrence of a positive indophenol-oxydase  
reaction in large, non-granular cells in acute leucæmia is a certain  
proof of their myeloid nature, and enables a diagnosis of acute  
myeloid leucæmia to be readily made from a blood examination.  
The reaction is negative in the more embryonic forms of marrow-  
cells, and in small myoblasts, and is probably always negative in  
the most typical stage of large myoblasts with uniformly dense  
basophil reticular protoplasm. When the reaction is positive in  
these large, non-granular cells, it is associated with alterations in  
the protoplasm, which are recognisable by ordinary staining

methods, and indicate stages of ripening towards the granular myelocytes. Cases of acute myeloid leucæmia may occur in which the type of blood-formation is so embryonic that the oxydase reaction is valueless for differential diagrams; but even in such cases the histological characters of the large leucocytes may render a diagnosis possible.

S. B. S.

Narcosis. BRUNO KISCH (*Zeitsch. Biol.*, 1913, 60, 399—456).—The action of photodynamic materials (eosin, methylene-blue) is increased in *Colpulia* by the addition of alcohol, ether, or chloroform. Dilute alcohol, however, acting for short periods, sometimes has the opposite effect so far as eosin is concerned. Narcosis in these animals is markedly affected by light. In *Spirostomum* the action of increased oxygen tension is increased by light, and there is a rise in the oxygen consumed in *Opalina*. The effect of light and oxygen on *Spirostomum* is inhibited by narcotics, but this is not seen in *Opalina*. The movements of these animals are paralysed by narcotics, but not in a reversible way.

W. D. H.

Gastric Juice in Malignant and Non-malignant Diseases of the Stomach and Duodenum. SAMUEL B. SCHRYVER and CHARLES SINGER (*Quart. J. Med.*, 1912, 6, 71—81; 1913, 6, 303—350).—Hans Fischer and Neuberg have suggested that the capacity of gastric juice to hydrolyse glycyl-tryptophan is diagnostic of cancer. The authors have investigated the action of gastric juices on Witte's peptone, and have shown, by the use of Sørensen's formaldehyde titration method, that in certain cases the gastric juice contains a peptolytic ferment. This was found in about 61% of the cases examined, all of which were taken from patients suffering from grave gastric disorder. It is only found when free hydrochloric acid is absent, and where the peptic powder is low, or even absent. It is not diagnostic of malignancy, as in the majority of cases of undoubted cancer the ferment was absent. It is most commonly associated with gastric dilatation and atrophy of the walls of the stomach, and is probably of intracellular origin.

Investigations were also carried out with the object of interpreting the analyses of gastric juice as regards the titration numbers obtained when methyl-orange and phenolphthalein are used as indicators. If  $B$  denotes the number of c.c. of  $N/10$ -sodium hydroxide necessary to neutralise 10 c.c. of gastric juice to phenolphthalein, and  $C$  the number of c.c. of alkali required to neutralise the same amount to methyl-orange, and  $A$  the number of c.c. of  $N/10$ -ammonia produced when 10 c.c. of the juice are incinerated by Kjeldahl's method with sulphuric acid, then  $(C - B)/A$  was found to be a constant for any given amino-acid or mixtures of amino-acids or digestion products.  $(C - B)/A \times 10$  has been designated the "nitrogen factor," and this is approximately a constant, and equal to about 2.4 for all cases of normal gastric juice. It is higher than that of gluten which has been digested for about one hour with pepsin in  $N/20$ -hydrochloric acid and pepsin of the same strength as that normally found in gastric juice, but is about equal to that



of a digest of an Ewald test-meal produced under similar conditions. The results indicate that the hydrochloric acid is not excreted in the form of an organic precursor. In cases of pyloric obstruction the "nitrogen factor" rises to 2.8 and more, and these high numbers are practically diagnostic for this condition. In cases of carcinoma of the body of the stomach, free mineral acid is absent, and pepsin is almost always absent, the analyses indicating almost complete achylia. In ulcers of the body of the stomach, the analyses vary, but complete achylia, such as is found in cases of carcinoma, is infrequent. Sometimes the analyses in this condition are not far removed from normal. In cancer of the pylorus, as opposed to cancer of the body of the stomach, the analyses are generally nearly normal; it is only when this condition is accompanied by distension and obstruction that the analytical numbers are sub-normal. The composition of the juice appears therefore to be affected rather by the site than the character of the lesion. Analytical numbers higher than normal are characteristic of pyloric and duodenal ulcers. Attention is called to the value of pepsin estimations, and to certain low values of the pepsin, when the hydrochloric acid secreted is normal or even high. For the purpose of pepsin estimation, the Fuld-Levison edestin method was employed. S. B. S.

**The Entrance of Iodine into Diseased Tissues.** H. GIBSON WELLS and O. F. HEDENBURG (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxxvi—xxxvii; *J. Biol. Chem.*, 14).—Necrotic tissues, whether caused by tuberculosis or not, are more permeable to iodine, and therefore contain more than healthy tissues when iodine is given. W. D. H.

**Pharmacological Investigations of Ammonium Chloride.** RODOLFO MENEGUZZI (*Chem. Zentr.*, 1913, i, 1016; from *Arch. Farmacol. sperim.*, 1912, 14, 411—420).—The injection of ammonium chloride into the veins of a rabbit caused a retardation in the pulse-beats and an increase in the blood pressure, whilst the breathing was quickened at first, but suddenly ceased. A 1/40N-solution had a toxic action on the fresh gastrocnemius of a frog, but weaker solutions were without effect. J. C. W.

**Behaviour of Mercury [in the Organism].** ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, 84, 67—68).—Polemical. Compare Buchtala (this vol., i, 318). E. F. A.

**The Injection of Salts of Radium.** HENRI DOMINICI, (Mme.) SIMONE LABORDE, and ALBERT LABORDE (*Compt. rend.*, 1913, 156, 1107—1109).—A study of the intravenous and intramuscular injection of soluble and insoluble salts of radium, which shows that they persist for a long time in the organism. In the case of the insoluble salts injected into the muscles the greater portion of the radium remains at the point of injection, whereas with the soluble salts it is diffused throughout the organism. The bony tissue retains an appreciable quantity of the radium injected as radium bromide, thus bringing radium into line with calcium and strontium in this respect. W. G.

**Thorium-X in Biology and Pathology.** J. PLESCH, LÁSZLÓ KARCZAG, and BRUNO KRETMAN (*Chem. Zentr.*, 1913, i, 318, from *Zeitsch. exper. Path. Ther.*, 1912, 12, 1-84).—The behaviour and distribution of thorium-X in the animal organism are described. The measurements were made by estimating the  $\alpha$ - or  $\gamma$ -radiation. About 80% is retained in the body, roughly two-thirds being stored in the bones, and most of the remainder in the liver. The toxicity varies considerably for different animals, and a lethal dose for a man is calculated at 10,000 electrostatic units, whilst a therapeutic dose should not exceed 1000 units. The symptoms accompanying the administration of thorium-X vary. The respiration of healthy subjects is not affected, but in cases of cardiac weakness or pneumonia the blood pressure is reduced. The preparation has a clinical application in metabolism, circulation and blood troubles, and in infectious diseases. J. C. W.

**Action of Thorium-X on the Circulation.** THEODOR A. MAASS and J. PLESCH (*Chem. Zentr.*, 1913, i, 318; from *Zeitsch. exper. Path. Ther.*, 1912, 12, 85-94).—Experiments on the isolated heart of a frog show that, like radium emanation, thorium-X increases the diastolic relaxation of the heart. J. C. W.

**Experimental and Histological Investigation of the Action of Thorium-X on the Animal Organism.** A. PAPPENHEIM and J. PLESCH (*Chem. Zentr.*, 1913, i, 318; from *Zeitsch. exper. Path. Ther.*, 1912, 12, 95-107).—The results of the action of thorium-X on the animal organism are to be referred to dilation of the blood vessels accompanied by bleeding and poisoning of the cells. Thorium-X is also a poison to the leucocytes of the marrow of the bones and to the kidney and liver epithelia. J. C. W.

**Pharmacological Differences between *cis*- and *trans*-Isomerides.** HEINRICH DRESER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 122-123).—The following figures give before the / the lethal dose, and after the / the dose which is no longer lethal, in the case of frogs (F) and white mice (M). The doses were injected under the skin, and are given in percentage-weights of the animal used. Atropic acid, F, 0.45/0.40; M, 0.0054/0.0022. Ordinary cinnamic acid, F, 0.30/0.25; M, 0.19/0.166. *allo*Cinnamic acid, F, 0.16/0.12; M, 0.2/0.175. *trans-o*Coumaric acid, F, 0.15/0.40; M, 0.30/0.278. *cis*Coumarinic acid, F, 0.084/0.0715; M, 0.01/0.0051. *trans-o*Methoxycinnamic acid, F, 0.20/0.15; M, 0.07/0.04. *cis-o*Methoxycinnamic acid, F, 0.7/0.5; M, 0.15/0.111.

The lethal doses are smaller for warm-blooded than for cold-blooded animals (compare atropic acid). The *cis*-isomeride is less poisonous than the *trans*-isomeride; the exception shown by coumaric and coumarinic acids is due to the fact that the latter gives the very poisonous coumarin in the organism. The introduction of phenolic hydroxyl into the ortho-position in *trans*-cinnamic acid decreases, whereas the methoxy-group increases, the toxicity.

The results show that no assumptions as to the pharmacological action of a substance can be based on chemical isomerism.

T. S. P.

**Pyruvic Acid Glycosuria. II. The Question of Sugar Formation from Pyruvic Acid.** PAUL MAYER (*Biochem. Zeitsch.*, 1913, 49, 486—501).—If pyruvic acid in suitable doses is administered to rabbits and dogs with total phloridzin diabetes, it causes an injury to the kidneys, which are rendered less permeable to nitrogenous substances and sugar. The administration in these cases results therefore in a diminution of both sugar and nitrogen in the urine. Even in cases where no injury to the kidneys could be ascertained, the administration of pyruvic acid led to no extra output of sugar. The experiments with animals with phloridzin diabetes offer, therefore, no solution of the problem as to whether pyruvic acid can be regarded as a sugar former in the body.

S. B. S.

**The Action of Methyl Alcohol on the Circulating Blood.** SOICHIRO MIURA (*Biochem. Zeitsch.*, 1913, 49, 144—151).—In two only out of five experiments (on four rabbits and one dog) did injection of methyl alcohol produce anæmia. There was observed a diminution of lymphocytes and an increase in the number of pseudo-eosinophile or neutrophile corpuscles and also hæmoglobinuria. The methyl alcohol appears to act toxically on the blood-forming apparatus.

S. B. S.

**Caffeine Hyperglycæmia.** THOR STENSTRÖM (*Biochem. Zeitsch.*, 1913, 49, 225—231).—It has been assumed that caffeine preparations produce glycosuria by acting on the kidneys. If this is the case, then no hyperglycæmia should result. The author now shows, by experiments on rabbits, employing Bang's microchemical method of sugar estimation, that administration of caffeine derivatives leads to increase of sugar in the blood, which commences about an hour after administration, rises to a maximum and then falls. In two cases, after the maximum period there was a second very rapid rise and fall, which was accompanied by convulsions in the animals, which subsequently died. The conclusion is drawn that the glycosuria produced by caffeine preparations is not due to the action on the kidneys.

S. B. S.

**The Behaviour of Dextrose-Resorcinol in the Animal Organism.** LUCIANO PIGORINI (*Chem. Zentr.*, 1913, i, 319; from *Arch. Pharmacol. experim.*, 1912, 14, 353—358).—The additive compound of dextrose and resorcinol (Fischer and Jennings, A., 1891, i, 397) is without harm to the frog or the guinea-pig, and is excreted unchanged, whereas resorcinol or mixtures of resorcinol and dextrose have a toxic action.

J. C. W.

**The Destruction of  $\alpha$ -Hydroxypropaldehyde and Methylglyoxal by Animal Organs.** CARL NEUBERG (*Biochem. Zeitsch.*, 1913, 49, 502—506).—It has been suggested that pyruvic

acid, as an intermediary product of sugar fermentation, can be formed by the Cannizzaro reaction from methylglyoxal. Equations are given showing that this substance can yield on hydrolysis (1) pyruvic acid and acetol, or (2) pyruvic acid and  $\alpha$ -hydroxypropionaldehyde, (3) pyruvic acid only. It was therefore of interest to investigate the behaviour of methylglyoxal and  $\alpha$ -hydroxypropionaldehyde when these substances are treated with various ferments from yeast or animal organs. Experiments show that with liver paste, both substances are destroyed, the former more rapidly than the latter. *p*-Nitrophenylhydrazine acetate was employed to detect their presence in the mixture, after the proteins had been precipitated by colloidal ferric hydroxide. More lactic acid was found in the incubation mixture than the organs alone would yield. The actual course of the reactions discussed has not, however, been yet entirely elucidated. S. B. S.

**The Behaviour of Ferric Iodoparanucleate in the Organism.** ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1913, 49, 152-164).—By the action of iodine on ferric paranucleate (triferrin), a product can be obtained which contains about 8% of organically combined iodine. It causes no toxic symptoms when administered to dogs and rabbits. On administration *per os*, the iodine, even in large doses, is completely absorbed into the system, whereas the iron is only partly absorbed. The iron content of the liver can be increased threefold after administration of iodotriferrin. No organically combined iodine could be detected in the body, after ingestion of the medicament, and the iodine appears to be excreted chiefly as alkali iodide, with a small quantity as an iodo-derivative of an aromatic acid. The iodine excretions last for three days after administration of the drug. S. B. S.

**Enzyme Concerned with the Formation of Hydroxy-acids from Ketonic Aldehydes.** HENRY D. DAKIN and HAROLD W. DUNLEY (*J. Biol. Chem.*, 1913, 14, 155-157).—Phenylglyoxal administered to rabbits in doses of 1-1.5 grams per kilo. leads to the excretion of about half a gram of optically active *l*-mandelic acid and about 0.75 gram of hippuric acid. No phenylglyoxylic acid was detected. Aqueous extracts of various animal tissues contain an enzyme capable of converting phenylglyoxal into mandelic acid, the action of which is readily inhibited by heat.

By analogy, methylglyoxal should be converted into lactic acid, and an enzyme extract prepared from dog's liver is shown to effect this change.

Phenylglyoxal readily combines with histidine, arginine, ornithine, and lysine to give sparingly soluble yellow substances. E. F. A.

**The Influence of Phloridzin on Dogs with Eck's Fistula.** JESSICA E. SWEET and A. I. RINGER (*J. Biol. Chem.*, 1913, 14, 135-138).—Phloridzin produces glycosuria in dogs with Eck's fistula exactly as in normal dogs. The power of glucosogenesis is not lessened.

W. D. H.

**The Influence of Phloridzin on a Splenectomised Dog.** JOSUEA H. AUSTIN and A. I. RINGER (*J. Biol. Chem.*, 1913, **14**, 139—140).—In dogs minus a spleen the effect of phloridzin exactly resembled those produced in normal animals. W. D. H.

**Lead Compounds in the Organism.** ANTONIO RIVA (*Chem. Zentr.*, 1913, i, 1047—1048; from *Arch. Pharmacol. experim.*, 1912, **14**, 406—410).—The lead-poisoned liver of a dog was extracted by physiological salt solution, and the filtrate, containing the albumins, globulins, and nucleoproteins, was evaporated to dryness. Lead was only found in the globulin, apparently in combination, since it persisted after repeated dialysis. A globulin from horse serum showed a great affinity for lead. J. C. W.

**The Action of Dyes in Conjunction with Poisons and Medicaments.** JOSEF SELLEI (*Biochem. Zeitsch.*, 1913, **49**, 466—478).—The mixture of dyes with poisons increases in many cases the toxicity of the latter, even although the dye is by itself practically inert. The dyes chiefly used were vitalnucgelb, chrysoidin, methyl-orange, etc., which were combined with, amongst other substances, mercuric chloride, gold chloride, platinum chloride, and other metallic chlorides. Sodium vanadate mixed with a certain quantity of eosin is very toxic, but an increase of eosin in the mixture above a definite limit appears to diminish the toxicity. Other combinations of dyes with metallic poisons are less toxic than the metallic poisons alone. The influence of methylene-blue on the toxicity of copper salts was investigated. The most toxic of these, namely, cupric chloride, loses its toxic power most readily on mixture with the dye, whereas potassium cupric tartrate, which is the least toxic, acts in the presence of methylene-blue most toxically. The mixtures of dyes with the copper salts produce convulsions in the animals (guinea pigs); they also act as strong irritants at the place of injection. The author discusses the theory of the action of dyes. S. B. S.

**Influence of Poisons on the Isolated Heart of the Fish.** W. I. BERESIN (*Flüger's Archiv*, 1913, **150**, 549—568).—The heart of the fish (hake) lends itself very well to physiological experimentation. Details are given of the method employed for isolating the heart, and the perfusion apparatus (a modification of Locke's fluid) employed. If poisons are added to the perfusion fluid (Locke's fluid) their effects are readily observable. The poisons used were strophantidine, erythrophycin, caffeine, adrenaline, nicotine, pilocarpine, chloroform, ether, hydrocyanic acid, quinine, and veratrine. The effects are practically identical with those already known from work on the heart of the frog or the mammal; a few differences of detail were noted in one or two instances. W. D. H.

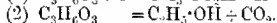
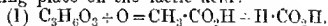
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## Chemistry of Vegetable Physiology and Agriculture.

The Phosphorus Compounds formed by *Amylomyces Rouxii*. R. GOURIL (*Compt. rend.*, 1913, 156, 959—962).—*Amylomyces Rouxii* contains combined phosphorus in three states, two organic and one inorganic. The organic compounds are normal constituents of the living tissue, and their formation corresponds with the period of active growth. Of these two compounds one only is soluble in, and extracted by, ether, and is of a lecithin-like nature, whilst the second, which can be extracted by sodium hydroxide and reprecipitation by acids, possesses all the properties of a nucleic acid, and appears to be built up from the lecithin compound. The inorganic phosphates result from the degradation of the organic phosphorus compounds as the plant grows old. W. G.

The Precipitation of Calcium Carbonate in the Sea by Marine Bacteria. G. HAROLD DREW (*J. Marine Biol. Assoc.*, 1913, 9, 479—524).—The large, chalky, mud flats forming the Great Bahama Bank, and those near the Florida Keys, are now being precipitated by the action of *B. calcis* on the calcium salts dissolved in sea water. This or similar bacteria may have been an important factor in the formation of various chalk strata and oolitic rocks in addition to the part played by shells of foraminifera, etc. If this is correct, these strata must have been precipitated in shallow seas at tropical temperature. Bacterial denitrification is also far more rapid in tropical than in temperate waters; hence plankton and alga growth is relatively scarce in the former. More extensive observations on the distribution of bacteria at different places and depths are, however, necessary. W. D. H.

Alcoholic Fermentation of Lactic Acid. PIERRE MAZÉ (*Compt. rend.*, 1913, 156, 1101—1104).—A study of the fermentation of lactic acid by a bacillus, capable of fermenting sugars and polyatomic alcohols, and comparable in its physiological properties to the *B. ethacetosuccinicus* of Frankland and Frew (T., 1892, 61, 254). An examination of the results points to two parallel fermentation processes taking place on the lactic acid:



The ratio of acetic acid to formic acid in the product is, however, as 5:1, the alcohol formed in (2) undergoing further oxidation, and this is confirmed by the value of the respiratory quotient. No pyruvic acid could be detected in any of the cultures at any stage.

W. G.

An Acid-producing Enzyme in *Bacterium lactis acidii*. E. G. HASTINGS and EDWIN B. HART (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxxviii—xxxix; *J. Biol. Chem.*, 14).—The enzyme in question acts on lactose, and the acid produced is probably lactic.

W. D. H.

**Employment of Lactic Acid and Lactic Acid Bacteria in the Pickling of Cucumbers.** ALEXANDER KOSSOWICZ [with L. VON GRÖBLER] (*Chem. Zentr.*, 1913, i, 640; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 2, 78-80).—The presence of small quantities of lactic acid in cucumber sap or asparagine-sugar solutions prevents the development of bacteria of the *Mesentericus* group. J. C. W.

**A New Thermophilic Bacterium.** ADOLF AMBROŽ (*Centr. Bakt. Par.*, 1913, ii, 37, 3-16).—A sporogenous, facultative anaerobic organism, *Denitrobacterium thermophilum*, was obtained from soil and found to have the capacity of growing vigorously at 60-70°, and of decomposing nitrates with the liberation of free nitrogen. Analysis of cultures in nutrient bouillon, containing 0.5% potassium nitrate, showed that about 25% of the total nitrogen was lost during an incubation period of fourteen days at 60-65°. The gases were found to consist of nitrogen and oxides of nitrogen, the former being partly derived from the organic nitrogen compounds in the bouillon. H. B. H.

**The Mechanism of Alcoholic Fermentation.** ALEXANDER VON LEBEDEV (*Ber.*, 1913, 46, 850-851).—Polemical. A reply to Kostytshevy (this vol., i, 323), stating that there is nothing essentially new in the latter's views. D. F. T.

**The Rate of Fermentation by Growing Yeast Cells.** ARTHUR SLATOR (*Biochem. J.*, 1913, 7, 197-203).—Various methods for estimating the rate of growth and fermentation are given, some of which are possible when the organism is growing on a solid medium. The rate of growth developing in wort-gelatin follows the logarithmic law. W. D. H.

**Chemical Composition and Formation of Enzymes. VIII. Simultaneous Variation in Amount of Invertase and Fermenting Enzyme in Living Yeast.** HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, 84, 97-108. Compare A., 1912, ii, 376, 970).—As the result of the previous treatment of the yeast in solutions containing mineral salts and sucrose or invert sugar there is an increase in the inverting power. This change cannot be regarded as an adaptation to environment, since the increase is the same whether the previous treatment is with sucrose or invert sugar. Neither is it due to a general increase in the vital activity of the cell, since the treatment materially lessens the fermentative activity. It is regarded as a special property due to causes as yet unknown. E. F. A.

**The Enzymes of Washed Zymin and Dried Yeast (Lebedev). I. Carboxylase.** ARTHUR HARDEN (*Bio.-Chem. J.*, 1913, 7, 214-217).—If zymin and Lebedev's dried yeast are washed free from co-enzyme they are incapable of fermenting dextrose, but they readily decompose pyruvic acid into carbon dioxide and acetaldehyde, provided that the acidity of the solution is kept low. W. D. H.

**Action of Free Ammonia on Yeast. Comparison with Other Bases.** THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 641—642; from *Allg. Brauer Hopfen Zeit.*, 1912, 52, 2867—2869).—Seeds of rye, barley, wheat, hemp and vetch, and peas and scarlet runners were allowed to germinate in ammonia solutions from 0.1 to 0.01%. Only at the lower dilution did germination proceed, and even then, at a slower rate than in control experiments. Ammonia to the extent of 0.5% in a good culture solution prevented the growth of yeast, whilst potassium hydroxide in the same dilution had no effect. Yeast apparently combines with ammonia, for it was found that 12 grams of yeast with a dry weight of 3.6 grams contained 0.374 gram of the base. Hydroxylamine and phenylhydrazine hydrochlorides were poisonous to yeast in 0.1% solutions, whilst hydrazine hydrate in 0.002% and phenylhydrazine in 0.001% solutions entirely prevented any fungoid growth. J. C. W.

**Microchemical Detection of Potassium in Yeast and Other Cells.** THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 640—641; from *Allg. Brauer Hopfen Zeit.*, 1913, 52, 113—114).—In order to make the potassium cobaltinitrite precipitate more visible it is blackened by means of ammonium sulphide. It is possible to detect one part of potassium in 5000 at 8° by this method. Potassium could only be found in the cell sap of yeast, but the conclusion is not to be drawn that it is not present in the protoplasm or nucleus in the form of a potassium protein compound. Potassium is necessary for the development of yeast. J. C. W.

**Action of Certain Metallic Salts on the Development of Yeast and the Germination of Barley.** THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 641; from *Allg. Brauer Hopfen Zeit.*, 1912, 52, 1905—1906).—The reproduction of yeast was not influenced by the presence of even 4% of potassium dihydrogen phosphate in the culture solution, neither did the ash contain more phosphorus. Cesium sulphate was found to be harmful to barley seedlings, even in the dilution of 0.05%, but 0.01% of that salt or 0.2% of rubidium sulphate proved to be beneficial, whilst potassium chloride in 0.05% solution did not accelerate germination, and in strong solutions was injurious. J. C. W.

**Action of Uranium, Molybdenum, and Vanadium Salts on Yeast and Other Micro-organisms.** THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 641; from *Allg. Brauer Hopfen Zeit.*, 1912, 52, 709—710. Compare A., 1912, ii, 1201).—During fermentations in presence of ammonium molybdate, the liquid acquired a blue colour, due to the action of that salt on hydrolysis products of sucrose, particularly on levulose. J. C. W.

**Influence of Different Substances on the Germination of Vegetable Seeds. I, II, and III.** THOMAS BOKORNY (*Biochem. Zeitsch.*, 1913, 50, 1—48, 49—86, 87—118).—Potassium chloride is somewhat injurious to plants in 0.25% solutions, whilst the nitrate



is very injurious in 1% solutions, and may retard growth even in 0.1% solutions. Calcium nitrate (1%) is only slightly injurious, and sodium nitrate somewhat more so; 0.1% solutions of both salts are without injurious effects. Even 0.1% solutions of ammonium nitrate retard germination. Whilst rubidium sulphate is only slightly injurious in 0.5% solutions, caesium and lithium sulphates are injurious in 0.1 and 0.05% solutions respectively.

Germination is quickened by caesium, lithium, and rubidium sulphates in 0.01, 0.05, and 0.2% solutions respectively. The germination of barley was promoted by 0.005% of carbon disulphide; beans and lentils by 0.01% potassium chromate; cress by 0.0005% mercuric chloride; barley and cress by 0.0025% and 0.005% copper sulphate respectively; cress by 0.005% of phenylhydrazine; barley and cress by 0.0025% of aniline; barley by 0.01% of hydroxylamine; and peas, lentils, and barley by 0.001% of hydrofluoric acid.

It would seem that most poisons stimulate growth when diluted to certain points. Since a slight increase in concentration causes injury and a slightly increased dilution renders the substances inactive, it is doubtful whether this property of poisons can have any practical importance.

N. H. J. M.

**Action of Manganese Dioxide and of Other Metallic Compounds on the Germination of Seeds.** UGO VARETTO (*Chem. Zentr.*, 1913, i. 546—547; from *Staz. sperim. agrar. ital.*, 1912, 45, 917—929).—The oxides of manganese, iron, uranium, cerium, copper, zinc, aluminium, cadmium, and mercury hinder the germination, of beans, and are poisonous, even in small doses, to horse beans. The oxides of zinc, lead, copper, cadmium, aluminium, and uranium are stimulants to maize.

J. C. W.

**Formation of Pentosans in the Germination of Seeds.** LUIGI BERNARDINI and F. GALLUCCIO (*Chem. Zentr.*, 1913, i. 179; from *Staz. sperim. agrar. ital.*, 1912, 45, 874—884).—The pentosans developed by seeds germinating in the dark and in the light have been estimated by Tollens's and Krüger's phloroglucinol method, and the cellulose by König's glycerol-sulphuric acid method. The results show that the production of pentosans is slow in the dark, but rapid in the light, whilst the cellulose content rises at first in the dark, only to fall off rapidly as germination proceeds, but increases steadily in the light.

J. C. W.

**Respiration of Plants as Hydrolytic Oxidation.** VLADIMIR I. PALLADIN (*Ber. deut. botan. Ges.*, 1913, 31, 80—82).—Alkaline solutions of the respiration chromogens absorb atmospheric oxygen vigorously with production of brownish-red pigments. During alcoholic fermentation, hence in the first anaerobic stage of respiration, substances are formed which readily give up their hydrogen to the respiration pigment, by which it is oxidised to water by means of atmospheric oxygen.

The respiration chromogens, like the leuco-compounds, give u

their hydrogen to the absorbed oxygen, producing a pigment and water. The oxygen absorbed during respiration is employed, therefore, as previously shown, in removing hydrogen from the plants.

The hydrogen liberated after the hydrolytic oxidation of dextrose, which in higher plants is oxidised to water and in yeast is eliminated as ethyl alcohol, is given up by anaerobic bacteria to the surrounding gaseous medium. N. H. J. M.

**Causes of Growth of Plants.** G. A. BOHOVIKOV (*Biochem. Zeitsch.*, 1913, 50, 119—128. Compare this vol., i, 324).—Salts which are readily hydrolysed are favourable to growth owing to the presence of acids, and consequently of hydrogen ions. The weaker the base the more easily is it hydrolysed, and the stronger the action of the salt. In solutions of salts of strong organic bases, growth is not quickened because hydrolysis is less, and because such bases have a greater retarding effect than weak bases, such as caffeine, carbamide, and glycine. The quickening or retarding of growth seems to be due to unequal degrees of hydration of the plasma colloids. The conditions which are favourable to the ionisation of the protein also bring about greater hydration of the plasma colloids. Acids are favourable to plants, whilst metals and bases diminish the protein ionisation by neutralising the protein. N. H. J. M.

**Formaldehyde and Plant Syntheses.** HERMANN DECKER (*Annalen*, 1913, 396, 336).—The hypothesis of the action of formaldehyde as a methylating agent in the formation of plant substances, advanced by Decker and Becker (this vol., i, 291), was suggested by Pietet eight years ago. C. S.

**Plants which Require Sodium.** WINTHROP J. V. OSTERHOUT (*Bot. Gaz.*, 1912, 54, 532—536).—Sodium was found to be as necessary for the marine plants employed as for animals, and its replacement in sea-water by ammonium, potassium, caesium, lithium, magnesium, calcium, and strontium is injurious. The best substitutes are the elements which predominate in sea water, magnesium, calcium, and potassium.

The behaviour of various species indicates that each salt has a specific action. N. H. J. M.

**Antagonistic Action of Chemical Substances on Fungi. Chemical Preservation.** THOMAS BOKORNY (*Cent. Bakt. Par.*, 1913, ii, 37, 168—267).—Numerous experiments are described on the action of various inorganic and organic substances on fungi, yeasts, etc. The results are summarised in tables. N. H. J. M.

**Assimilation of Nitrites by Moulds.** ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1913, i, 640; from *Zeitsch. Gärungsphysiol. Mikologie*, 1912, 2, 55—58).—Ten moulds have been found to subsist with nitrites as their source of nitrogen, and since in only two cases could ammonia be detected, the conclusion is drawn that the

nitrite ion is assimilated directly, without reduction. In good culture media, moderate concentrations of nitrites are not poisonous to moulds.

J. C. W.

**Decomposition of Carbamide, Uric Acid, Hippuric Acid, and Glycine by Moulds.** II. ALEXANDER KOSOWICZ (*Chem. Zentr.*, 1913, i, 640; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 2, 51—55).—Several of the well-known moulds are able to make glycine or hippuric acid their sole source of nitrogen in presence of mannitol or dextrose, some of them producing ammonia. Certain moulds can depend on uric acid, hippuric acid, or glycine for their combined source of carbon and nitrogen.

J. C. W.

**Chemistry of the Higher Fungi. IX. Galls Produced by *Exobasidium Vaccinii*, Woron., on *Rhododendron ferrugineum*, L.** JULIUS ZELLNER (*Monatsh.*, 1913, 34, 311—319. Compare A., 1912, ii, 196).—The galls and the leaves on which they are found have been examined, and shown to contain the same constituents, the former containing a larger proportion of water-soluble substances, except tannin, and a smaller proportion of matter insoluble in water, than the leaves. On this and other grounds, it is suggested that the formation of galls on leaves is similar in character to the production and ripening of fruits.

The galls and the leaves were extracted in turn with light petroleum, ether, 95% alcohol and water, and the composition of these extracts was as follows: The galls yielded 1.71% to light petroleum; the product was a thick, semi-crystalline oil, having acid number 93.4, saponification number 165.1, and containing 12.5% of unsaponification matter, composed of (a) a substance, m. p. 129—130°,  $[\alpha]_D^{25}$  -29.4°, crystallising in colourless needles, and (b) a substance, m. p. above 280° (decomp.), much less soluble than the foregoing; both these products are phytosterols. The fatty acids of the oil are semi-solid. The leaves yielded 9.2% to light petroleum; the extract had acid number 60, saponification number 150, and contained the same two phytosterols as the gall extract, and also much resin and terpenes.

The ether extract of the galls amounted to 2.68%, and consisted of tannin and resin. The leaves yielded 8.34% to ether, and this extract also consisted of tannin and resin, the latter being somewhat different from that in the galls.

The alcohol extract of the galls amounted to 39.1%, and consisted of phlobaphen, dextrose, levulose, tannin, and organic acids. The leaves yielded 32.6% to alcohol, and this extract consisted chiefly of tannin with some phlobaphen and a small amount of sugar.

The aqueous extract of the galls amounted to 13.32%; it contained some tannin, but was mostly gummy carbohydrate; no starch was present. The leaves gave only 1.7% of aqueous extract of similar composition to the foregoing, but containing some starch.

All the foregoing yields are expressed as percentages of the original material dried at 100°.

T. A. H.

Chemistry of the Higher Fungi. X. JULIUS ZELLNER (*Monatsh.*, 1913, 34, 321-336).—In this portion four fungi are dealt with, the method of investigation being the same as that described in the preceding abstract.

*Armillaria mellea*, Vahl.—The light petroleum extract was a semi-crystalline, thick, brown oil, having acid number 89.1, saponification number 179.6, iodine number 94.2, and containing notable amounts of lecithin and 4.5% of unsaponifiable matter, the latter consisting of a yellow resin and some ergosterol. The fatty acids were mostly liquid, but yielded when kept a mixture of crystalline acids, m. p. 62°, and acid number 210°. The ether extract contained some amorphous matter and ergosterol, m. p. 155°,  $[\alpha]_D^{25}$  -114.8° in chloroform, which gave an acetyl derivative, m. p. 169°. No cerebrin was found. The alcoholic extract deposited after a time mannitol, m. p. 169-170° (possibly contaminated with mycose), dextrose, choline, and matter precipitated by lead acetate.

*Lactarius piperatus*, L. (compare Thörner, A., 1880, 44; Bissinger, A., 1884, 480; Chodat and Chuit, A., 1890, 80; Gérard, A., 1891, 606; and Bougault and Charaux, A., 1912, ii, 289).—The light petroleum extract amounted to 5.9%, and was a solid, yellow fat, having acid number 121.3 and saponification number 200.2. The unsaponifiable matter was separated into (1) a substance, m. p. 146-150°, probably a mixture of ergosterols; (2) a yellow resin; and (3) a sparingly soluble substance, m. p. 150° (approx. decomp.). This extract also contained lecithin. The fatty acids included some liquid acids, but the principal constituent was stearic acid, which was isolated in quantity (*loc. cit.*). The ether extract amounted to 1.2%, and consisted of yellow resin. The alcoholic extract contained mannitol (possibly contaminated with inositol), dextrose, and choline (compare Bourquelot, A., 1890, 103).

*Pholiota squarrosa*, Müll.—The light petroleum extract (3.8%) was a semi-solid, yellowish-brown fat, having acid number 51.8, saponification number 168.3, containing lecithin and 12.9% of unsaponifiable matter. From the latter a resin and a mixture of ergosterols, m. p. 159 (approx.), crystallising in colourless leaflets, were isolated. The ether extract resembled the foregoing in composition. The alcoholic extract contained mannitol, mycose, dextrose, choline, phlobaphen, and indefinite amorphous matter soluble in alcohol, but not in water.

*Polyporus betulinus*.—The light petroleum extract amounted to 3.5%, and had acid number 96.3, saponification number 155.0, iodine number 98.6, and contained 17.8% of unsaponifiable matter composed of a mixture of ergosterols, m. p. 139-141°,  $[\alpha]_D^{25}$  -97.6°, crystallising in needles or leaflets, cerebrin, resin, and gum. The ether extract was resinous, and contained a substance,  $C_{21}H_{38}O_5$ , m. p. 250° (approx. decomp.), which is probably an alcohol and is named *polyporal*. The alcoholic extract contained phlobaphen, mannitol, dextrose, traces of choline, and indefinite substances precipitated by lead acetate and other salts. The aqueous extract contained potassium phosphate and a carbohydrate, giving a pale

greyish-blue coloration with iodine, and readily hydrolysed by dilute hydrochloric acid. Winterstein's paraosodextran (A., 1895, i, 323) could not be obtained.  
T. A. H.

**Extraction of the Colouring Matter from the Cherry and Investigations of its Properties.** GIULIO MASONI (*Chem. Zentr.*, 1913, i, 546; from *Staz. sperim. agrar. ital.*, 1912, 45, 885—907).—The pigment may be extracted from fresh or dried cherries by means of water or alcohol with the help of a little tartaric or hydrochloric acid. The aqueous extract may be cleared by gelatin, and is violet-red and not very stable, whereas the alcoholic extract is clear, pure red in colour, and remains unaffected by heat or light. The dye may be applied to wool or food-stuffs. Its presence in wine may be detected, after clearing the liquid with lead acetate, by the addition of alum, when a violet coloration is produced, pure wines remaining colourless.  
J. C. W.

**Chemical Examination of Euphorbia pilulifera.** FREDERICK R. POWER and HENRY BROWNING, jun. (*Pharm. J.*, 1913, [iv], 36, 506—516).—A complete chemical examination of the entire plant, collected in Fiji, has been made. None of the definite constituents isolated has any specific physiological action, so that such therapeutical value as the plant possesses cannot depend on any single definite substance. An alcoholic extract of the plant was steam-distilled, and yielded (1) a volatile oil, b. p. 235—260°, giving the colour reaction of furfuraldehyde; (2) a portion soluble in water; (3) a resinous portion, insoluble in water; the two latter portions of the extract were then examined by methods which are described in detail, and gave the following products:

*Portion Soluble in Water.*—This yielded gallic acid, quercetin, a small amount of jambulol (see also below), and a phenolic substance,  $C_{28}H_{12}O_8$ , which crystallised in microscopic clusters of needles, and decomposed, but did not melt, at 340°. There was also present a levorotatory sugar, which yielded *d*-phenylglucosazone, some amorphous glucosidic matter, traces of an alkaloidal substance, together with indefinite oily and extractive matters.

*Portion Insoluble in Water.*—This yielded melissic acid, ceryl alcohol, triacontane, a *phytosterol*, m. p. 132—133°, crystallising in flattened needles, and giving an *acetyl* derivative, m. p. 122—123°; a *phytosterolin*,  $C_{33}H_{56}O_6$ (?), m. p. 297° (decomp.), crystallising in colourless needles, and yielding an *acetyl* derivative, m. p. 161—162°, crystallising in flattened needles; jambulol (T., 1911, 99, 962, and A., 1912, ii, 480), and a mixture of palmitic, oleic, and linoleic acids. In addition, a monohydric alcohol, *euphosterol*,  $C_{25}H_{39}OH$ , m. p. 274—275°, was obtained. This crystallises from petroleum in needles, gives the colour reaction characteristic of this class of substances (T., 1909, 95, 739; 1912, 101, 2425), and is optically inactive. It yields an *acetyl* derivative, m. p. 295—297°.  $[\alpha]_D + 8.2^\circ$  in chloroform, and this on bromination in cold chloroform gives *bromoacetyleuphosterol*, m. p. 183—186°, crystallising in small needles from a mixture of alcohol and ethyl acetate.

Euphosterol is probably accompanied by other alcohols of the same series, since in recrystallising the acetyl derivative two other fractions, m. p. 205—210° and m. p. 230—260°, were obtained.

T. A. H.

**Causes of the Natural Changes in the Latex of *Hevea Brasiliensis*.** G. STAFFORD WHITBY (*Z-tschr. Chem. Ind. Kolloide*, 1913, 12, 147—157).—Experiments are described which have been made in order to ascertain the nature of the changes which are involved in the coagulation of the latex of *Hevea Brasiliensis* when this is left in contact with the air. The observations indicate that coagulation is brought about by an enzyme (probably a protease). Anaerobic decomposition occurs in those portions which are out of contact with the air, and evidence has also been obtained which indicates the presence of an oxydase, to which the name, *hevease*, is applied.

A fourth factor in the coagulation process consists in aerobic decomposition, which occurs in the later stages, and gives rise to an alkaline mucus which causes the latex to become milky. The relative importance of these four independent processes depends very largely on the conditions under which coagulation of the latex occurs.

H. M. D.

**Herbage Studies. II. Variation in *Lotus Corniculatus* and *Trifolium repens* (Cyanophoric Plants).** HENRY E. ARMSTRONG, E. FRANKLAND ARMSTRONG, and EDWARD HORTON (*Proc. Roy. Soc.*, 1913, B, 86, 262—269).—It is established that in addition to the common widely distributed cyanophoric form of *Lotus corniculatus*, a botanically indistinguishable form exists, in which the power of producing the cyanophoric glucoside is all but suppressed. *Lotus major* is uniformly cyanophoric. The normal form of *L. corniculatus* contains both glucoside and the correlated enzyme, a second form is rich in enzyme, but contains mere traces of the glucoside, whilst in the third form the amount of both glucoside and enzyme is very small.

The conclusion is drawn that the above differences are due to the presence or absence of definite factors rather than the consequence of the operation of special conditions of environment.

Whereas cultivated white clover (*Trifolium repens*) is without cyanide, wild white clover always contains a cyanophoric glucoside.

The determination of the enzymic activity of a number of specimens of *Trifolium repens* showed that all were moderately active towards salicin, but that the cultivated variety alone was practically without action on linamarin and prunasin.

The bearing of the chemical peculiarities of the two types of clover on their value as food materials is discussed. E. F. A.

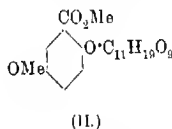
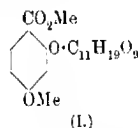
**Chemistry of Peat Moss (*Sphagna*).** JOSEF IBELE (*Ber. deut. bot. Ges.*, 1913, 31, 74—77).—When *Sphagnum papillatum* is oxidised with hydrogen peroxide a substance soluble in sodium hydroxide

solution is obtained, which becomes insoluble when precipitated with acid and dried. Formic acid and ammonia are also formed.

Sphagnum dissolves almost completely in hydrochloric acid containing antimony trichloride. Ammonia is liberated, but no methylamine could be detected.

N. H. J. M.

**Glucosides and Oils of the Primrose.** A. GORIS, M. MASOURY, and CH. VISCHNIAC (*Chem. Zentr.*, 1913, i, 310—311; from *Bull. Sci. Pharmacol.*, 1912, 19, 577—598, 648—670; *Wiss. ind. Ber. Rouve. Bertrand fils*, 1912, 6, 3—73. Compare A., 1910, ii, 63).—The crude glucosides which form about one part per thousand of the roots of *Primula officinalis* may be separated by fractionation from a mixture of ethylacetate and alcohol. Primverin (I),  $C_{25}H_{28}O_{13}$ , m. p. 206° (corr.),  $[\alpha]_D - 71^{\circ}53'$ , yields on hydrolysis with dilute acids, methyl  $\beta$ -methoxyresorcylate,  $C_9H_{10}O_4$ , m. p. 49°, which develops a violet-red colour with ferric chloride, and two molecular proportions of monoses. The enzyme primverase, however, produces the biase, *primverose*,  $C_{11}H_{20}O_{10}$ , m. p. 209—210°, which exhibits multirotation;  $[\alpha]_D + 23^{\circ}11'$ ,  $-2^{\circ}3'$  after twenty-four hours (1.846 grams in 75 c.c.  $H_2O$ ),  $+23^{\circ}11'$ ,  $-3^{\circ}17'$  after twenty-four hours (1.35 grams in 26 c.c. of water). It reduces Fehling's solution (0.0673 gram = 77 mg. Cu), forms an *osazone* in light yellow needles, m. p. 204—207°, and contains a pentose, apparently in combination with a hexose.



Primulaverin,  $C_{20}H_{24}O_{13} \cdot 2H_2O$ , m. p. 163° (corr.),  $[\alpha]_D - 66^{\circ}65'$ , yields on hydrolysis the same sugars and methyl *m*-methoxyresorcylate, mixed with methyl  $\beta$ -methoxyresorcylate. It has not yet been obtained pure, but the true primulaverin would have the formula II.

The ethereal oils of the primrose root contain the above esters, whilst the oil from the flowers contains, in addition, over 10% of an unhydrolysable substance.

J. C. W.

**Willow Bark. I.** GEORGEI GEORGEVITSCH POVARNIN and A. BARABANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 267—271).—The authors have examined the barks of a number of willows, including hybrids, with the object of classifying them according to their chemical reactions. Tannides of two distinct types occur in the barks (see following abstract).

T. H. P.

**Willow Bark. II.** GEORGEI G. POVARNIN and N. SIBIRIALEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 271—283. Compare preceding abstract).—The bark of the hybrid willow, *Salix alba*  $\times$  *S. viminalis*, contains, in addition to phlobaphens, two tannides which are char-

acterised by their reactions with ferric chloride and with ammoniacal copper sulphate. The tannide of *S. alba* is a tannoside, and may be separated from that of *S. viminalis*, which contains free sugar, by its different solubility in a mixture of methyl alcohol and ether. The former gives anhydro- and oxy-phlobaphens, and it contains protocatechuic acid, whilst the tannide of *S. viminalis* contains pyrogallol, but the principal decomposition products are phlobaphen and sugar.

T. H. P.

**Manuring of Cultivated Plants by means of Carbon Dioxide.** ADOLPH HANSEN (*Chem. Zentr.*, 1912, ii, 2135; from *Naturw. Rundsch.*, 1912, 27, 547—550).—It was noticed that the vegetation in the neighbourhood of a natural carbonic acid spring was particularly fine, and the administration of carbon dioxide to cultivated plants is found to increase the dry weight considerably. It is suggested that the gas is loosely combined with the chlorophyll in the same way as oxygen is united to the pigment of the blood.

J. C. W.

**Importance of the Potassium in Felspar for Plants.** EDWIN BLANCH (*J. Landw.*, 1913, 61, 1—10. Compare *ibid.*, 1912, 60, 97).—Pot experiments in which oats were manured with various potassium minerals. Previous results, indicating that the tubes are more suitable as sources of potassium for plants, are confirmed.

Plagioclase gave much better results than microclin and orthoclase, which were almost without effect.

N. H. J. M.

**History of Maize Sugar.** PH. DE VILMORIN and FERDINAND LEVALLOIS (*Bull. Soc. chim.*, 1913, [iv], 13, 294—304).—The authors give an extensive review of the efforts which have been made to extract a crystallisable sugar from maize on the industrial scale, special reference being made to the work of Pallas and to the recent investigations of Stewart and of Heckel (*Compt. rend.*, 1912, 155, 686).

A series of experiments have been made on maize from Verrières and from Antibes, the conditions, however, being rather unfavourable. In these circumstances, the juice from maize from which the ears had been removed during growth was found to contain 10% of sucrose, whilst a greater proportion could be extracted from sugar maize. From the industrial point of view, the extreme rapidity, both of formation and of decomposition of sugar in maize, constitutes a serious difficulty, which, however, could possibly be obviated to some extent by the systematic employment of different varieties of maize.

H. W.

**Respiration and Metabolism in Ruminants.** NATHAN ZUNTZ, RICHARD VON DER HEIDE, KLEIN, I. VON MARKOFF, FÜRST VON DESCHANDIERI, and DJADKOW (*Landw. Versuchs-Stat.*, 1913, 79-80, 781—814).—The utilisation of foods by cattle varies according to the mechanical condition of the mixture, and the same food will give different results when given in conjunction with other foods. An experiment is described in which potatoes were compared with



the corresponding amount of potato slump to which starch was added to replace that which had been lost; whilst malt and yeast were added to the potatoes. Although the two foods had practically the same composition, the results with starch were essentially different from those with potatoes. When starch is given in conjunction with hay, the crude fibre, protein, and fat are digested in diminished amounts. In the case of the non-nitrogenous extract the amount in the faeces was diminished by the starch. This does not, however, indicate better resorption, as there is no doubt that the extractive substances were lost by fermentation. The comparison of food and faeces is misleading in the case of ruminants.

It is desirable in feeding experiments to estimate the amount of oxygen utilised as well as the amounts of respired nitrogen and carbon dioxide. A method for estimating the oxygen is described.

The various estimations in respiration experiments should be made at short intervals.

Methods for investigating the fermentation processes of the rumen are discussed.

N. H. J. M.

Employment of Dialysis in the Estimation of the Oxidising Power of Soils. JOSEF KÖNIG, JULIUS HASENBÄUMER, and K. GLENK (*Landw. Versuchs-Stat.*, 1913, 79-80, 491--539).—Several soils were subjected to dialysis, and the amounts of organic matter, calcium, magnesium, potassium, phosphoric acid, and sulphuric acid in the solutions estimated. It was found that soils which were heated at 150° yielded considerably more soluble matter than soils which had not been heated; similar results, but less marked, were obtained with soils dried, under reduced pressure, at 95—98°. Clearer indications of the changes which soils undergo when heated, and even when air-dried, were obtained by estimating the electrolytic conductivity. The results indicate that in the ordinary drying of soils the colloidal state is in part destroyed.

The amounts of carbon dioxide produced in six different soils, and in the same soils with small amounts of dextrose and urea respectively, were estimated daily for three weeks; and at the end of the experiment the amounts of ammonia and nitrates and the numbers of bacteria were estimated (compare Hutchinson and Marr, A., 1911, ii, 430). As regards nitrification, the urea was almost completely nitrified in the loamy soil, whilst the clay soil showed very slight nitrification. Addition of dextrose considerably increased the number of bacteria in all the soils. Electrolytic conductivity was increased by urea and diminished by dextrose.

The results of pot experiments with oats showed that heating the soil at 95—98° in a vacuum increased both the total growth and the mineral constituents. Addition of dextrose and gum arabic to loamy sand and loam diminished the yield of grain and straw.

N. H. J. M.

Colloidal Substances in Soil Solutions. Production of Soda in Soils. Alkali and Salt Soils. K. K. GEDROIZ (*Bied. Zentr.*, 1913, 42, 76—79; from *J. exper. Landw.*, 1912, 13, 421).—The amount of colloids in soil extracts (except alkali soil extracts)

was found to vary from 0.0018 to 0.0200%, and in Russian arable soils from 0.0058 to 0.0147%. The dry matter dissolved by water amounted to 0.0385 to 0.0591%. The coagulation of such small amounts of colloidal substances can have very little effect on the physical properties of the soils; and the changes brought about by frost, electrolytes, and liming, etc., are attributed to their influence on substances mechanically suspended in the soils, especially the gels.

In the case of alkali soils the total colloids, mineral and organic, varied from 0.0990 to 0.4494%; in such soils coagulation of the colloids may influence the physical properties of the soil.

In typical alkali soils, nearly free from chlorides and sulphates, the amount of soda in successive extracts decreases much more slowly than would be the case if only pre-existing soda were dissolved. In alkali soils containing much sodium chloride, but little sulphate, alkalinity begins only after some of the chloride is washed out.

A loamy, black soil, treated with sodium chloride and calcium carbonate, failed to yield appreciable amounts of soda, and only small amounts were produced by treatment with sodium sulphate and calcium carbonate. Under the combined influence of sodium chloride and sulphate, alkaline, dark-coloured solutions were obtained after the removal of most of the chloride and sulphate; in presence of calcium carbonate the soil yielded soda. The conclusion is drawn that the soda is produced from zeolites. The production of soda is hindered by excessive amounts of sodium chloride and sulphate.

N. H. J. M.

**The Fertilising Action of Sulphur.** A. DEMOLON (*Compt. rend.*, 1913, 156, 725—728).—Further experiments with sulphur (compare A., 1912, ii, 382) show that it can act as a useful addition to farmyard manure as a fertiliser, but that its action diminishes and vanishes in the presence of a large amount of organic and mineral fertilisers. Potatoes benefit most by the addition of sulphur. On light lands it has an injurious effect on cereals. Addition of sulphur in amount equal to the nitrogen supplied has given the same results as a complete mineral fertiliser. The fertilising action of the sulphur is due (a) to its action on the soil bacteria, (b) to its progressive transformation into sulphuric acid.

W. G.

**[Manurial] Action of Different Forms of Nitrogen.** W. SCHNEIDEMUND (*Bied. Zentr.*, 1913, 42, 101—110; from *Arch. d'ent. Lond.-ges.*, Heft. 217).—Pot and field experiments on the action of sodium and calcium nitrates, calcium nitrite, ammonium salts, calcium cyanamide, and urine. On the whole the best results were obtained with sodium and calcium nitrates. Ammonium salts were not regular in their action; in one case, both on dry and wet soils, ammonium salts gave better results than nitrate. Both with oats and potatoes, nitrates and ammonium salts gave the same results. Calcium cyanamide acted most favourably when applied in the autumn for winter cereals. Urine was unsatisfactory both on light and loamy soils. The effect of calcium nitrite was variable.

The application of large amounts of manure to light soils in the autumn is useless; ammonium salts and calcium cyanamide may, however, be applied to soils of better quality. N. H. J. M.

**Influence of Ammonium Sulphate on the Phosphate Manuring of Oats.** EILHARD A. MITSCHERLICH and W. SIMMER-MACHER (*Landw. Versuchs-Stat.*, 1913, 79-80, 71-96).—Addition of ammonium, sodium, and magnesium sulphates considerably increased the solubility of the phosphoric acid of di- and tri-calcium phosphates, whilst in presence of calcium phosphate the solubility is diminished.

The results of vegetation experiments, in which oats were manured with di- and tri-calcium phosphates, showed that the addition of small amounts of ammonium sulphate increased the amounts of phosphoric acid assimilated even in presence of considerable amounts of soluble salts which would be acting in the same direction.

In the case of superphosphate and basic slag, addition of ammonium sulphate was without effect on the assimilation of the phosphoric acid by oats. N. H. J. M.

**Manuring with Sodium Salts.** BERNHARD SCHULZE (*Landw. Versuchs-Stat.*, 1913, 79-80, 431-448).—Sodium is utilised by plants, and may take the place of potassium to a certain extent. The sodium of sodium chloride is taken up by plants with great rapidity; and, as it is not absorbed by soils to the same extent as potassium, its manurial action lasts longer if not washed out of the soil.

Whilst potassium salts decompose sodium zeolites in the soil, sodium salts have a very slight action, if any at all, on potassium zeolites. N. H. J. M.

**Lime Rich in Silica as Manure.** HEINRICH IMMENDORFF (*Landw. Versuchs-Stat.*, 1913, 79-80, 891-901).—Different soils were rubbed in a mortar with lime and water, and then put on to glass plates to dry in order to ascertain whether any hardening of the soil takes place owing to the presence of silica. The limes employed contained from 0.03 to 19.51% of soluble silica (Portland cement). The same soils were treated with water alone for comparison.

The results showed that no hardening of the soil takes place when lime containing large amounts of soluble silica are employed. Hydrated silica may itself have a favourable effect on the soil by increasing its absorptive power. N. H. J. M.

## Organic Chemistry.

Composition of Mineral Oils of High Boiling Point. I. The Viscous Components of Mineral Oils of High Boiling Point. JULIUS MARCUSSEN (*Chem. Zeit.*, 1913, 37, 533—534).—Previous investigations (*ibid.*, 1911, 35, 729) have shown that the more viscous portion of mineral oils (naphthenes, polynaphthenes, paraffins, and olefines) is that which does not react with formaldehyde and sulphuric acid, whilst the reacting portion (benzene derivatives, unsaturated naphthenes, and terpenes) is comparatively mobile. Paraffins have small viscosity, whilst that of naphthenes is greater than that of paraffins of the same molecular weight. The viscosity of mineral oils cannot therefore be attributed to the presence of paraffins. This is confirmed by the fact that the viscosity of lubricating oils can be raised by removal of solid paraffins and lowered by their addition. Olefines are present in too small amount to exert a distinct effect on the viscosity, so that the diminution in viscosity effected by treating oils with fuming nitric acid at  $-10^{\circ}$  must be attributed to the destruction of polynaphthenes. The viscosity must therefore be due to the presence of naphthenes and polynaphthenes. The former are mainly present in the portions distilling below  $300^{\circ}$ , so that in oils of high b. p. and high viscosity, the chief saturated hydrocarbons are polynaphthenes. This is confirmed by analysis of a heavy Russian machine oil, which, before purification, contained C=85.79% and H=12.78%, whilst after treatment with formaldehyde and sulphuric acid, the figures obtained were C=85.41%, H=13.07%, which correspond with the results to be expected from a mixture of condensed naphthenes. Further confirmation is found in the high molecular weight of machine oils, which ranges from 300 to 400 with a mean value of about 350, corresponding with compounds containing twenty-five atoms of carbon in the molecule.

Highly viscous oxygen compounds are present in nearly all machine oils, but, generally, in such small amount that their effect is inconsiderable.

The present communication deals only with machine oils. Cylinder oils are under investigation. H. W.

Composition of Mineral Oils of High Boiling Point. II. Components of Liquid Paraffin and their Behaviour towards Aluminium Chloride. JULIUS MARCUSSEN and C. VIELTIZ (*Chem. Zeit.*, 1913, 37, 550—553).—The so-called liquid paraffin is generally regarded as a mixture of liquid hydrocarbons of the paraffin series. This view, however, appears improbable, since the substance is usually obtained from Russian oils which are comparatively poor in such hydrocarbons.

Two specimens of liquid paraffin were employed, having  $D_4^{20}$  0.8827, 0.8858,  $n_D^{20}$  1.4797, 1.4799, specific viscosity at  $20^{\circ}$ , 23.0, 29.9,

$[\alpha]_D^{20}$  +2.13, 2.35, respectively. The density and refractive index indicate that hydrocarbons of the paraffin series cannot be the main components of the mixture, whilst ultimate analysis points to the presence of polynaphthenes.

In order to decide whether the optical activity is attributable to isoparaffins or polynaphthenes, a specimen of liquid paraffin was fractionated under greatly reduced pressure. Density, viscosity, refractive index, and optical activity were found to increase with increasing b. p. of the fraction. Since the fraction, b. p. 255--277.4 mm., was completely liquid and only yielded a trace of precipitate when cooled with alcohol-ether to  $-20^\circ$ , it appears improbable that isoparaffins can be the cause of activity. This is confirmed by the results of an ultimate analysis, and further by the fact that optical activity is not lost when liquid paraffin is subjected to energetic treatment with fuming nitric acid. Activity must therefore be due to the presence of polynaphthenes, which is in accord with the observation of Bushong and Humphrey (*Chem. Zeit.*, 1912, 36, 1139) that optically active naphthenic acids are present in mineral oil.

The optically active constituents of liquid paraffin are stable towards fuming sulphuric or fuming nitric acid, but are readily inactivated by aluminium chloride. When a solution of liquid paraffin in carbon disulphide was heated on the water-bath during three hours with aluminium chloride and the residue left after removal of the solvent was extracted with light petroleum, a colourless oil was obtained, which possessed feeble optical activity and considerably lower density, refractive index, and viscosity than the original material. From that portion of the reaction product which was insoluble in light petroleum, a viscous, brown substance was obtained, solutions of which were too deeply coloured to permit polarimetric observation. In the absence of any solvent, similar inactivation was observed. With light petroleum as solvent, however, the recovered oil had nearly the same properties as the original specimen. This difference is probably attributable to the fact that the yellowish-white additive product formed from liquid paraffin and aluminium chloride is practically insoluble in light petroleum, whilst it is appreciably soluble in carbon disulphide and also in liquid paraffin. In the first case, therefore, the liquid paraffin becomes practically protected from further action of aluminium chloride.

Finally, a series of experiments has been performed on the action of aluminium chloride on different optically active substances dissolved in carbon disulphide. Campher and castor oil were not affected. Resin oil, oil of turpentine, cholesterol, and the unsaponifiable portions of wool grease yielded black masses from which optically inactive products were extracted by light petroleum. H. W.

**Structure of Acetylene.** ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, 17, 320--321. Compare this vol. ii, 494).—The total number of valencies in acetylene calculated from the critical data by the author's formula is ten. The formula of acetylene at its critical point is therefore  $H-C\equiv C-H$ , and not  $C\equiv C H_2$ . R. J. C.

**Preparation of  $\beta$ -Dihalogen *iso*Pentanes by the Chlorination of  $\beta$ -Halogen *iso*Pentane.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 257600).—When the vapours of monohalogenated tertiary *isopentanes* are treated with chlorine (or bromine), they readily furnish a satisfactory yield of the technically important  $\beta$ -dihalogen *isopentanes*, and the preparation of  $\beta$ -dichloro*isopentane*, b. p.  $60^\circ/60$  mm., from  $\beta$ -chloro*isopentane* is described. F. M. G. M.

**The Preparation of Carbon Tetraiodide.** MARCEL LANTENOIS (*Compt. rend.*, 1913, **156**, 1385—1387).—A critical study of the various methods recommended for the preparation of carbon tetraiodide (compare Spindler, A., 1886, 434; Moissan, A., 1891, 1420; Robineau and Rollin, A., 1895, i, 123). The author adopts Spindler's method, but prefers to replace the calcium iodide with lithium iodide, which gives a very pure product on heating it with excess of carbon tetrachloride in a vacuum in a sealed tube at  $90-92^\circ$  for five days. The best solvents for carbon tetraiodide are benzene, acetone, and carbon disulphide. W. G.

**Higher Tertiary Alcohols Derived from Palmitic and Stearic Esters.** HUGH RYAN and THOMAS DILLON (*Proc. Roy. Irish Acad.*, 1912, **B**, 29, 235—245).—A series of tertiary alcohols has been prepared by the action of Grignard's reagents on esters of palmitic and stearic acid. The latter were readily obtained by the addition of a few c.c. of concentrated sulphuric acid to a hot solution of the acid in excess of the requisite alcohol, the yields in every case being more than 90% of the quantity theoretically obtainable. The following esters were obtained in this manner: methyl palmitate, needles, m. p.  $28^\circ$ ; ethyl palmitate, long needles, m. p.  $24.2^\circ$ ; *n*-propyl palmitate, needles, m. p.  $18.8-19.2^\circ$ ; methyl stearate, needles, m. p.  $38^\circ$ ; ethyl stearate, needles, m. p.  $31^\circ$ ; *n*-propyl stearate, prisms, m. p.  $28.6^\circ$ .

For the preparation of tertiary alcohols, the solid ester was added in small portions to an ethereal solution of the necessary Grignard's reagent. There were thus obtained: dimethylpentadecylcarbinol,  $C_{15}H_{31}O$ , needles, m. p.  $35^\circ$ ; diethylpentadecylcarbinol, curved needles, m. p.  $34-35^\circ$ ; diphenylpentadecylcarbinol, prisms, m. p.  $47-48^\circ$ ; dimethylheptadecylcarbinol, needles, m. p.  $44-45^\circ$ ; diethylheptadecylcarbinol, needles, m. p.  $44-45^\circ$ ; dipropylheptadecylcarbinol, needles, m. p.  $28-30^\circ$ ; diphenylheptadecylcarbinol, long, curved needles, m. p.  $58^\circ$ . The action of an ethereal solution of magnesium naphthyl bromide on methyl stearate led to the formation of *naphthyl heptadecyl ketone*,  $C_{17}H_{33}.CO.C_{10}H_7$ , m. p.  $55^\circ$ .

Diethylheptadecylcarbinyl acetate was obtained as an oily liquid, which solidified when placed in iced water, by the action of acetyl chloride on diethylheptadecylcarbinol.

Dimethylpentadecylcarbinol, when heated on the sand-bath with sodium acetate and acetic anhydride, yielded a mixture of the corresponding acetate and unsaturated hydrocarbon. A similar result was obtained with diethylheptadecylcarbinol.

Dimethylheptadecylcarbinol was apparently not affected when heated with potash-lime at  $250^\circ$ . At  $300^\circ$ , however, unsaturated substances

were produced, but no evolution of hydrogen was observed. Diphenylheptadecylcarbinol similarly yielded unsaturated substances at 300°.

H. W.

**Basic Properties of Oxygen. II.** OTTO MAASS and DOUGLAS McINTOSH (*J. Amer. Chem. Soc.*, 1913, 35, 535—543).—In an earlier paper (A., 1912, i, 825) it has been shown that the compounds formed by the union of halogens or halogen hydrides with organic substances containing oxygen differ in many respects from molecular aggregates containing water or alcohol of crystallisation. In order to ascertain whether such compounds exist in solution, conductivity determinations have been made of the two-component systems of hydrochloric acid with ethyl and methyl ethers and with ethyl and methyl alcohols over the complete concentration range at -89°. The results are compared with the freezing-point curves of the different systems. In the case of methyl ether, two compounds are formed, namely,  $\text{Me}_2\text{O} \cdot \text{HCl}$  and  $\text{Me}_2\text{O} \cdot 4\text{HCl}$  (?). With ethyl ether, three compounds are produced:  $\text{Et}_2\text{O} \cdot \text{HCl}$ , m. p. -92°;  $\text{Et}_2\text{O} \cdot 2\text{HCl}$ , m. p. -88°; and  $\text{Et}_2\text{O} \cdot 5\text{HCl}$ , m. p. -89°. Methyl and ethyl alcohols each yield only one compound, namely,  $\text{MeOH} \cdot \text{HCl}$ , m. p. -62°, and  $\text{EtOH} \cdot \text{HCl}$ , m. p. -65°. The conductivity curves indicate the probability of the existence of compounds in solution.

E. G.

**A Derivative of Quinquevalent Tungsten.** ARTHUR FISCHER and LOUIS MICHELS (*Zeitsch. anorg. Chem.*, 1913, 81, 102—115). Compare this vol., ii, 513).—The electrolysis of a solution of tungsten hexachloride in absolute alcohol gives at the platinum cathode a green, crystalline compound,  $\text{C}_6\text{H}_{16}\text{O}_9\text{Cl}_5\text{W}$ . It is decomposed by hot alcohol, but may be recrystallised from a mixture of alcohol and chloroform at 60°, cooling in ice. The compound forms bright green leaflets, with metallic lustre and slight fluorescence. It is slowly decomposed by hot water, yields the blue oxide when strongly heated, and gives the iodoform reaction. More than two-thirds of the carbon is evolved on heating in the form of ethylene. Oxidation with permanganate indicates that the tungsten is quinquevalent. The reactions indicate the composition  $\text{WCl}_5(\text{OEt})_5$ , but the molecular weight is double this, and the exact constitution is uncertain.

C. H. D.

**Catalytic Actions of Colloidal Metals of the Platinum Group. IX. The Hydrogenation of Egg-lecithin.** CARL PAAL and HERMANN OENNE (*Ber.*, 1913, 46, 1297—1304).—As in previous experiments with certain fats (A., 1908, i, 599; 1909, i, 358), so also it has been found possible to reduce egg-lecithin to a crystalline substance. Merck's reddish-brown, wax-like egg-lecithin had the iodine value, 55.3, but the volume of hydrogen absorbed in presence of colloidal palladium in 90% alcoholic solution was higher than this value would predict, being about 59 c.c. instead of 48.4 c.c. per 1 gram. The *hydrolecithin* partly separates from the solution, and may be recrystallised from chloroform and acetone as a white powder which sinters at 83—84°. On hydrolysis with barium hydroxide, it gave glycerol, phosphoric acid, and choline, which was identified as the

aurichloride, whilst the fatty acids recovered from the soap were found, after fractional crystallisation, to contain chiefly stearic acid, which would arise from the unsaturated  $C_{18}$ -acids of egg-lecithin. The presence of small quantities of acids of lower molecular weight, probably myristic, decolic, or lauric acids, showed that the substance and consequently the starting material were not quite homogeneous. Egg-lecithin is, however, chiefly a palmityl-linoly-llecithin, and the analysis of the hydrolecithin agreed fairly well with  $C_{42}H_{88}O_2NP$ , the formula of a palmityl-stearyl-lecithin.

J. C. W.

**Uranyl Formate.** GASTON COURTOIS (*Bull. Soc. chim.*, 1913, [iv], 13, 449—454).—The properties of *uranyl formate*,  $(HCO)_2UO_2 \cdot H_2O$ , which is obtained in non-deliquescent, yellow octahedra by digesting the hydrated oxide,  $UO_3 \cdot H_2O$ , with dilute formic acid at  $80^\circ$ , are very different in many respects from those described by Echsner de Coninek and Raynaud (this vol., i, 333). When crystallised from ice water, it still contains  $1H_2O$ , and it is not dehydrated by prolonged sojourn in a vacuum desiccator. When dried in this manner, it is stable up to  $100^\circ$ , loses water at  $150^\circ$ , but also formic acid. A moist sample loses water and formic acid at  $100^\circ$ , and becomes insoluble. The solubilities are 7.2% in water at  $15^\circ$ , 4.9% in methyl alcohol at  $18^\circ$ , only slightly soluble in concentrated formic acid or alcohol, insoluble in other organic media.

The concentrated solution slowly deposits a *basic salt* in the cold and dark, quickly on boiling, in the form of yellowish-white, truncated prisms of the composition  $(HCO)_2UO_3 \cdot H_2O$ ,  $UO_3 \cdot 2H_2O$ . Prolonged boiling with water results in the acid,  $UO_3 \cdot H_2O$ . When exposed to light for some time, dilute solutions of the formate gradually deposit this basic salt mixed with a small amount of a violet hydrate of uranoso-uranyl oxide. Even in methyl alcohol no brown uranyl oxide was obtained, but the above violet substance, which was transformed into the pale yellow oxide,  $UO_3 \cdot 2H_2O$ , in the air, and into the yellowish-white acid,  $UO_3 \cdot H_2O$ , on boiling with water.

J. C. W.

**Molecular Association of Acetic Acid.** EMILE BAUD (*Bull. Soc. chim.*, 1913, [iv], 13, 435—438).—According to the surface tension measurements of Ramsay and Shields (A., 1894, ii, 179), acetic acid exists in double molecules at the ordinary temperature. This was found to be the case when the acid is mixed with some organic solvents (A., 1912, ii, 233, 331, 1147), and is again confirmed by cryoscopic measurements in nitro- and chloro-benzene. The fact holds good even for strong solutions, from which it follows that the pure acid is bimolecular, and that the solvent has no associating influence in these cases.

Formic acid, however, like water, has a dissociating effect and the unimolecular value is obtained. The freezing-point curve for mixtures of the two acids does not indicate the formation of a compound, but it is assumed that combination does take place, since the heat absorbed on mixing the two substances is much less than the heat of dissociation of the double molecules. An equilibrium between the double molecules



and the mixed molecules,  $(C_3H_5O_2)_2 + (CH_2O_2)_2 \rightleftharpoons 2(C_2H_4O_2, CH_3O_2)$ , would require that in a dilute solution of acetic acid in formic acid, the acetic acid molecule would produce two molecules of the mixed acid and cause an excessive depression of the freezing point, leading, therefore, to the unimolecular value for the molecular weight.

J. C. W.

**Margaric Acid and its Relations to Palmitic and Stearic Acids.** ROBERT F. RUTAN (*8th Inter. Cong. Appl. Chem.*, 1912, 25, 431—442).—The history of margaric acid is related, a method of preparing the acid by the Grignard reaction is described, and the chief constants of the acid are recorded in comparison with those of palmitic and stearic acids.

When cetyl iodide is treated with magnesium in ether, in presence of iodine as a catalyst, micaceous crystals of the organo-magnesium compound separate. If the mixture is then treated with carbon dioxide, a mixture of ditriacontane and margaric acid is formed, the yield of the acid being 50% of the theoretical under the best conditions, which include the use of dry reagents throughout the operations. A method for the separation of the hydrocarbon and acid is described. Margaric acid crystallises in colourless, bulky, shining plates, melts at  $59.9-60^\circ$  (corr.), and solidifies at  $58.8^\circ$ . It has D 0.8532 at its melting point,  $n = 1.4342$  at  $60^\circ$ , and the coefficient of expansion is  $6.65 \times 10^{-4}$  at  $60-80^\circ$ . The following quantities (grams) dissolve in 100 grams of dry alcohol at the temperatures named:  $0^\circ$ , 1.53;  $5.4^\circ$ , 2.42;  $10^\circ$ , 4.12;  $15^\circ$ , 6.72;  $21^\circ$ , 13.4;  $28^\circ$ , 32.14. Methyl margarate, m. p.  $29^\circ$ , forms waxy scales. Ethyl margarate, m. p.  $27.5^\circ$ , crystallises in waxy plates. *Ethylene margarohydrin*, m. p.  $53.2^\circ$ , forms pearly scales, and *ethylene dimargarate*, m. p.  $70.4^\circ$ , glistening plates.

T. A. H.

**Saponification of Triglycerides.** JULIUS MEYER (*Chem. Zeit.*, 1913, 37, 541—542).—The author criticises the experiments of Fortini (A., 1912, i, 826) on the saponification of triolein with alkali hydroxide in alcohol. The latter found that the curves obtained by plotting (1) quantity of triglyceride hydrolysed against time, or (2) acetyl number against time, were composed of three parts corresponding with (a) formation of diglyceride; (b) formation of monoglyceride, and (c) formation of free fatty acid.

According to the author, the amount of alkali consumed is not a measure of the quantity of triglyceride saponified, since a portion of it is used in decomposing di- and mono-glycerides (compare Kellner, A., 1909, i, 357, 548, 759). Also, by plotting alkali consumed against time, a continuous curve is obtained in the saponification of triacetin in homogeneous solution by 0.01 and 0.02*N* potassium hydroxide (Meyer, A., 1909, ii, 803). Further, the determination of the acetyl number after definite intervals of time is not a satisfactory method of following the course of the reaction, since, particularly with the unsaturated oleic acid and its glycerides, this number depends greatly on the conditions under which the determination is executed, and is further complicated by the decomposition of the triglyceride into oleic

acetate and glycerol occurring with intermediate formation of di- and mono-glycerides (compare Kremann, A., 1905, ii, 630; 1908, i, 120; Fanto and Stritar, 1908, i, 499). H. W.

**The Behaviour of Paints Under the Conditions of Practice, with Special Reference to the Aspersions Cast on Lead Paints.** HENRY E. ARMSTRONG and C. A. KLEIN (*J. Soc. Chem. Ind.*, 1913, 32, 320—331).—This communication is, to a great extent, critical and polemical against the work of Baly (*The Oil and Colour Trades Journal*, 1911, 1518; A., 1912, i, 533), and the report of Breton in connexion with lead paints. The experimental part deals with the formation of volatile products from linseed and other oils and the ordinary materials used in making paints, and with the test for lead in the volatile products, if any, from paint materials. The leaf of the common shrub, *Aucuba Japonica*, or the spotted Japanese laurel, is used as a test for volatile products, in the presence of which it blackens more or less rapidly.

The conclusions arrived at are: The vapours produced during the drying of white-lead pastes and paints do not contain lead. The vapours given off as paints dry consist of turpentine for the most part, together with oxidation products of the oil; the latter are common to paints generally containing oil so treated that it will dry. The oxidation products formed from the oil during drying are harmless under the conditions of practice. The toxic effects sometimes experienced from drying paints are to be ascribed to turpentine; in many cases effects which have been regarded as due to lead-poisoning are attributable to other causes, especially to turpentine. The dangers attending the use of lead compounds are only the well-known mechanical dangers. T. S. P.

**Cerebronic Acid.** II. PHÆBUS A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1913, 14, 257—266. Compare A., 1912, i, 936).—Previous work indicated that cerebronic acid has the structure of an  $\alpha$ -hydroxypentacosic acid; on reduction the acid formed a hydrocarbon, m. p. 54—57°. According to Kraft and Marie, *n*-pentacosane has m. p. 53·5—54°. The experiments were repeated with a larger supply of material, and the melting point came out at the latter figure. By reduction of the acid,  $C_{25}H_{50}O$ , obtained by oxidation of cerebronic acid, a hydrocarbon, melting at 51—52°, was obtained, which is the melting point of normal tetracosane. Cerebronic acid is a  $\alpha$ -hydroxy-*n*-pentacosic acid.

*Acetylcerbronic acid*,  $C_{25}H_{48}O_3$ , obtained by the action of acetic anhydride on cerebronic acid, is a white, crystalline solid, m. p. 55·5—56°, and solidifies at 53—51°. W. D. H.

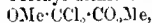
**Formation of  $\beta$ -Ketone Esters by the Application of Reformatsky's Reaction.** TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1913, 35, 582—585).—Fittig and Dainler (A., 1887, 361) have shown that ethyl chloroacetate reacts with ethyl oxalate in presence of amalgamated zinc with formation of ethyl ketipate. Reformatsky, in his work on the synthesis of dibasic hydroxy-acids (A., 1896, i, 206)

found that ethyl  $\alpha$ -bromopropionate reacts with ethyl formate with production of ethyl  $\beta$ -hydroxy- $\alpha\alpha$ -dimethylglutarate, but he obtained no evidence of the formation of ethyl formylpropionate corresponding with Fittig and Daimler's ethyl ketipate. In attempting, however, to prepare ethyl  $\beta$ -hydroxyglutarate from ethyl formate and ethyl chloroacetate (A., 1899, i, 516), he obtained ethyl trimesate as the chief product of the reaction, this having been formed by a condensation of ethyl formylacetate. The production of ethyl formylacetate and ethyl ketipate are analogous, and represent the first stage of Reformatsky's synthesis.

These results suggested that perhaps other esters besides ethyl formate and ethyl oxalate might undergo similar condensations with esters of halogen-substituted acids, and this has been found to be the case. The reaction has been applied to ethyl ethoxyacetate, ethyl  $\alpha$ -ethoxypropionate, ethyl bromoacetate, and ethyl  $\alpha$ -bromopropionate, and the following esters have been obtained: *Ethyl  $\gamma$ -ethoxyacetoacetate*,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $110^\circ/20$ — $21$  mm.,  $116$ — $126/26$ — $27$  mm.,  $120$ — $125^\circ/30$  mm., and  $130$ — $136^\circ/45$  mm. *Ethyl  $\gamma$ -ethoxy- $\alpha$ -methylacetoacetate*,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , b. p.  $113$ — $116^\circ/18$ — $20$  mm., and  $116^\circ/24$  mm. *Ethyl  $\gamma$ -ethoxy- $\gamma$ -methylacetoacetate*,  $\text{OEt}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $110$ — $115^\circ/19$  mm. *Ethyl  $\gamma$ -ethoxy- $\alpha\gamma$ -dimethylacetoacetate*,  $\text{OEt}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , b. p.  $108$ — $115^\circ/16$  mm. E. G.

#### Real and Supposititious Oxalomalonic Esters and Applicability of Methanetricarboxylic Ester for Synthetic Purposes

ROLAND SCHOLL and WILHELM EGERER (*Annalen*, 1913, 397, 301—366). The triethyl oxalomalonate (ethyl ketoethanetricarboxylate) and corresponding acid described by Kurrein (A., 1905, i, 413) are a mixture of ethyl oxalate and malonate, and a mixture of hydrated oxalic acid and malonic acid respectively. Also the substance, b. p.  $220^\circ/10$  mm., obtained by Bouveault in 1898 from ethyl sodiomalonate and ethyl oxalic chloride, and described by him as triethyl oxalomalonate,  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , cannot be this compound, as the sequel proves. [With EMIL HETSEN.]—Methyl dichloromethoxyacetate,



which is obtained in 80—90% yield by heating methyl oxalate and phosphorus pentachloride ( $1\frac{1}{2}$  mols.) at  $130$ — $135^\circ$  for thirty hours, is converted into methyl chloropyruvate,  $\text{CO}_2\text{Me}\cdot\text{COCl}$ , to the extent of 60% by heating it with a small quantity of platinum black in a bath at  $200^\circ$  until the temperature cannot be raised above  $140$ — $160$ ; the methyl oxalic chloride, b. p.  $117$ — $118^\circ$ , is then removed by distillation, and the residue again heated, a quantity of platinum black being again added if necessary.

Methyl sodiomalonate and methyl chloropyruvate in equal molecular quantities react in dry ether in a freezing mixture to form methyl malonate and *methyl dioxalomalonate* (*methyl  $\alpha\gamma$ -diketopropion- $\alpha\beta\gamma$ -tetracarboxylate*),  $\text{C}(\text{CO}_2\text{Me})_2(\text{CO}\cdot\text{CO}_2\text{Me})_2$ ; after the removal of the ether by a current of air at  $25^\circ$ , the residue is vigorously shaken with ice-water, by which all products are dissolved except the tetracarboxylate.

*Methyl dioxalomalonnate*, m. p. 97.5—98°, colourless needles or prisms, which can be also prepared in a similar manner from methyl chloropyruvate and methyl sodio-oxalomalonnate (see below), is unattacked by alkaline potassium permanganate or by bromine, and is therefore not an *O*-derivative,  $\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Me})_2\cdot\text{C}(\text{OMe})\cdot\text{O}\cdot\text{CO}\cdot\text{CO}_2\text{Me}$  or  $\text{C}(\text{CO}_2\text{Me})_2\cdot\text{C}(\text{CO}_2\text{Me})\cdot\text{O}\cdot\text{CO}\cdot\text{CO}_2\text{Me}$ ,

but is a very reactive substance in other ways. It is decomposed by water, slowly at the ordinary temperature and rapidly by heating, into oxalic acid and methyl malonnate. It is decomposed in the same manner by boiling methyl alcohol, with or without potassium hydroxide. Ammonia, phenylhydrazine, and aniline also decompose the tetracarboxylate, producing methyl malonnate and oxamide, oxalic acid diphenylhydrazide, or methyl oxanilate respectively.

By heating at 180—200°, methyl dioxalomalonnate loses carbon monoxide and is converted into *methyl oxalomethanetricarboxylate* (*methyl ketoethanetetracarboxylate*),  $\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Me})_2$ , m. p. 91—92°, b. p. 285—286° or 179—180°/15 mm., colourless plates, which is also prepared by heating methyl chloropyruvate and methyl sodiomethanetricarboxylate in benzene (see below). The ester is remarkably stable when heated, being almost unchanged after boiling for one and a-half hours. It does not give a coloration with alcoholic ferric chloride. When boiled with methyl alcohol, the ester is rapidly converted into methyl oxalate and *methyl methanetricarboxylate*,  $\text{CH}(\text{CO}_2\text{Me})_2$ , m. p. 45—46°, b. p. 22.7° (corr.) or 128°/15 mm., colourless prisms. Methyl methanetricarboxylate is also obtained by heating a suspension of methyl oxalomalonnate in benzene with methyl chloroformate; it is soluble in dilute sodium hydroxide or carbonate, and forms with methyl-alcoholic sodium methoxide a *sodio*-derivative,  $\text{C}_2\text{H}_3\text{O}_6\text{Na}$ , colourless needles. Methyl methanetricarboxylate exists as the ketonic modification in the crystalline state, but when fused or in alcoholic solution it is partly changed to the ondic form, since the reddish-brown coloration produced by ferric chloride gradually becomes more intense.

Many attempts have been made to prepare methyl oxalomalonnate (*methyl ketoethane  $\alpha\alpha\beta$ -tricarboxylate*) from methyl sodiomalonate and methyl chloropyruvate under different conditions of temperature and concentration, but the principal product is always methyl dioxalomalonnate. The desired ester, however, has been obtained from methyl dioxalomalonnate by careful decomposition with methyl alcohol or methyl sodiomalonate. The preparation is difficult because methyl oxalomalonnate itself is decomposed into methyl oxalate and methyl malonnate by methyl alcohol. A 10% solution of methyl dioxalomalonnate in benzene is kept with an equal molecular quantity of methyl alcohol for thirty days at the ordinary temperature, or at least four days at 50°, the product is distilled under about 12 mm. pressure, and the ethereal extract of the residue is fractionally crystallised, whereby *methyl oxalomalonate*,  $\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Me})_2$ , m. p. 49—50°, colourless needles, is obtained, the yield being about 50% of the amount ascertained volumetrically (see below). The ester is also obtained by treating a suspension of methyl sodiomalonate (2 mols.) in benzene at 50° with methyl dioxalomalonnate (1 mol.), removing the yellow precipitate (*sodio*-derivatives of methyl oxalomalonate and methyl

malonate), suspending it in ether at  $0^{\circ}$ , and treating it with dilute sulphuric acid at  $0^{\circ}$ ; the ester is obtained from the ethereal solution. A third method of preparing methyl oxalomalonate from methyl sodiomalonate and methyl chloropyruvate is described.

Methyl oxalomalonate forms colourless solutions in aqueous sodium hydroxide or carbonate, and does not react in ether with sodium. At  $120$ – $130^{\circ}$  it decomposes quantitatively into carbon monoxide and methyl methanetricarboxylate, and thus reacts as the ketonic modification. By titration with alcoholic bromine and  $\beta$ -naphthol by Meyer's method, it is shown that the ester is entirely enolic in alcohol or benzene, but contains about 7%, 21%, and 94% (?) of the ketonic modification in chloroform, acetone, and glacial acetic acid respectively. Meyer's method can also be employed to show that the maximum (molecular) percentage of methyl oxalomalonate obtained from equal molecular quantities of methyl alcohol and methyl dioxalomalonate in benzene (at  $18^{\circ}$  or at  $50^{\circ}$ ) is about 71%.

The series of ethyl esters corresponding with the preceding methyl esters has been prepared. Ethyl sodiomalonate and ethyl chloropyruvate react in ether to form ethyl malonate and a mixture of ethyl oxalo- and dioxalo-malonates, from which the latter cannot be isolated. By distillation under 15 mm. pressure, the mixture decomposes, evolves carbon monoxide, and produces ethyl methanetricarboxylate,  $\text{CH}(\text{CO}_2\text{Et})_3$ , m. p.  $28.5$ , and ethyl oxalomethanetricarboxylate,  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Et})_2$ , b. p.  $191$ – $192/15$  mm. (Bouveault's so-called ethyl oxalomalonate).

By treating an ethereal solution of the preceding mixture of ethyl oxalo- and dioxalo-malonates with sodium, ethyl sodio-oxalomalonate,  $\text{C}_{11}\text{H}_{15}\text{O}_7\text{Na}$ , is obtained as a white precipitate, from which ethyl oxalomalonate, D $^{15}$  1.1147, is obtained. Ethyl oxalomalonate is soluble in dilute sodium hydroxide or carbonate, but is not attacked by sodium except in the presence of a little ethyl malonate. It develops a red coloration with alcoholic ferric chloride, decomposes by heating into carbon monoxide and ethyl methanetricarboxylate, and is decomposed by water or phenylhydrazine in the same manner as the methyl ester.

Ethyl dioxalomalonate,  $\text{C}(\text{CO}_2\text{Et})_2(\text{CO}\cdot\text{CO}_2\text{Et})_2$ , is obtained from ethyl chloropyruvate and ethyl sodio-oxalomalonate in ether, and decomposes by heating.

Conrad and Guthzeit, Michael, and others have tried to utilise methanetricarboxylic esters for synthetic purposes. Their efforts have been unsuccessful, since they used alcohol, by which alkyl methanetricarboxylates are decomposed into alkyl malonates. In the absence of alcohol, alkyl sodiomethanetricarboxylates can be used for synthetic purposes as effectively as ethyl sodioacetacetate or sodiomalonate, higher temperatures, however, being necessary.

Diethyl ethyl methanetricarboxylate,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CO}_2\text{Me})_2$ , prepared from methyl sodiomalonate and ethyl chloroformate, has b. p.  $210$ – $241^{\circ}$ , or  $138$ – $139/12$  mm., and forms with sodium ethoxide a white sodio-derivative. Ethyl sodiomethanetricarboxylate reacts with methyl iodide at  $146^{\circ}$  to form ethyl ethane- $\alpha\alpha$ -tricarboxylate  $\text{CMe}(\text{CO}_2\text{Et})_3$ , b. p.  $250^{\circ}$ , or  $130/11$  mm., and with ethyl iodide, in a

similar manner, to form *ethyl propane-aaa-tricarboxylate*,  $\text{C}(\text{CO}_2\text{Et})_3$ , b. p.  $258^\circ$ , or  $146^\circ/17$  mm.; the latter ester, which has a bitter taste, is converted into ethyl carbonate and ethyl sodioethylmalonate by alcoholic sodium ethoxide.

Ethyl sodiomethanetricarboxylate and acetyl chloride react, finally on the water-bath, to form *ethyl acetylmethanetricarboxylate* (*ethyl  $\beta$ -ketopropane-aaa-tricarboxylate*),  $\text{C}(\text{CO}_2\text{Et})_2\text{COMe}$ , b. p.  $253^\circ$  or  $147-148^\circ/14$  mm., and with benzoyl chloride to form *ethyl benzoylmethanetricarboxylate*,  $\text{C}_{17}\text{H}_{20}\text{O}_7$ , b. p.  $214^\circ/14$  mm. Methyl sodiomethanetricarboxylate and methyl chloroformate react at  $120^\circ$  to form *methyl methanetetra-carboxylate*,  $\text{C}(\text{CO}_2\text{Me})_4$ , m. p.  $74-75^\circ$ , h. p.  $265^\circ$  (corr.)/735 mm., or  $163^\circ/12$  mm., colourless, tasteless needles, which is not attacked by alkaline potassium permanganate or by bromine, and is converted into malonic acid by dilute sulphuric acid and into methyl carbonate and methyl sodiomethanetricarboxylate by alcoholic sodium methoxide. *Dimethyl diethyl methanetetra-carboxylate*, b. p.  $293^\circ$ , or  $167^\circ/11$  mm., and *ethyl methanetetra-carboxylate*, m. p.  $13-5^\circ$ , b. p.  $304^\circ$  (corr.)/735 mm., or  $173-5^\circ/12$  mm., D<sub>4</sub><sup>20</sup> 1.0886, both of which have a bitter taste, are also described.

Ethyl oxalomethanetricarboxylate (see above) is also obtained from ethyl sodiomethanetricarboxylate and ethyl chloropyruvate in benzene. C. S.

**Effect of Heating Paraformaldehyde with a Trace of Sulphuric Acid.** JOHN G. M. DUNLOP (*Proc. Camb. Phil. Soc.*, 1913, 17, 180-181).—When a mixture of paraformaldehyde and sulphuric acid is heated at  $115^\circ$  in a sealed tube, bent in such a manner that one end is heated while the other end is kept cool by immersion in a beaker of water, a mobile distillate is obtained, which, when fractionated, yields methyl formate and a liquid, b. p.  $95-96^\circ$ , still under investigation, which appears to be a polymeride of formaldehyde. The yield of methyl formate is very variable and depends on the amount of sulphuric acid and also on the temperature. With about six drops of sulphuric acid to ten grams of trioxymethylene, a yield of about one to two grams of ester appears to be usual. With five grams of acid to the same weight of trioxymethylene, great charring takes place and practically no ester is formed. H. W.

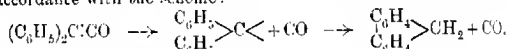
**Methylation of isoValerone by means of Sodamide and Methyl Iodide.** Tetramethylisovalerone or  $\beta\gamma\gamma\epsilon\zeta$ -Hexamethylheptan- $\delta$ -one. ALBIN HALLER and EDUARD BÄGER (*Compt. rend.*, 1913, 156, 1295-1298. Compare this vol., i, 485).—By the action of sodamide on isovalerone dissolved in benzene, followed by addition of methyl iodide according to the usual method, a liquid was obtained which, after twice repeating this methylation, gave, on fractional distillation,  $\beta\gamma\epsilon\zeta$ -tetramethylheptan- $\delta$ -one, b. p.  $76-78^\circ/13$  mm., yielding only traces of an oxime, and  $\beta\gamma\gamma\epsilon\zeta$ -pentamethylheptan- $\delta$ -one, b. p.  $88-89^\circ/13$  mm., which gave no oxime, and was not decomposed on boiling with sodamide in benzene. The last substance on further methylation with sodamide and methyl iodide in toluene yielded  $\beta\gamma\gamma\epsilon\zeta$ -hexamethylheptan- $\delta$ -one, b. p.  $107-109^\circ/14$  mm., which gave

neither oxime nor semicarbazone, and was not decomposed by sodamide in boiling toluene. On reduction with sodium in alcohol, it yielded the corresponding  $\beta\gamma\gamma\epsilon\epsilon'$ -hexamethylheptan- $\delta$ -ol, b. p. 115—117°/13 mm., giving a phenylurethane, m. p. 91—92°. W. G.

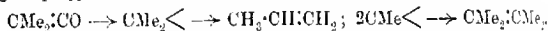
**Reactions of Methylene. IV. The Decomposition of Ketens at High Temperature.** HERMANN STAUBINGER and R. ENDLE (*Ber.*, 1913, 46, 1437—1442. Compare A., 1912, i, 245).—Since it has been shown (this vol., i, 604) that dicarbon dioxide is incapable of existence, but decomposes into carbon monoxide with rupture of the ethylenic bond, whilst, generally, ethylene derivatives are remarkably stable towards heat, the authors have been led to examine the behaviour of ketens at high temperatures, as these substances form an intermediate link between dicarbon dioxide and the true ethylene derivatives.

The experiments were performed in a quartz tube closed at one end at which the substance was placed. In the middle of the tube a silver spiral was placed which could be maintained at 600—700°. The tube was further connected with a suitable condensing arrangement. Previous to an experiment the tube was exhausted. The substance was then vaporised, and the vapours conducted over the heated spiral.

Diphenylketen, when heated in the above manner, yielded fluorene in accordance with the scheme:



Dimethylketen, obtained by heating tetramethyldiketocyclobutane, gave propylene and tetramethylethylene:



In similar circumstances, diphenylethylene and tetraphenylethylene were not altered, whilst only slight decomposition occurred with diphenyldichloroethylene. Diphenylmethane also underwent no change. At 250°, diphenylbromomethane was converted into tetraphenylethylene and hydrogen bromide. When the silver spiral was replaced by fragments of porcelain, diphenylbromomethane and diphenylchloromethane yielded at 700° tetraphenylethylene instead of fluorene, so that possibly the course of the reaction depends on the contact material.

Phenylcarbimide and phenylthiocarbimide were not affected by a silver spiral at 700°, or by a platinum spiral heated to glowing.

II. W.

**Esterification of Dihydroxyacetone with Phosphates.** ALEXANDER VON LEBEDEV (*Zeitsch. physiol. Chem.*, 1913, 84, 305).—Polemical (compare Euler and Johansson, A., 1912, i, 750).

E. F. A.

**The Action of Ultraviolet Light on Sucrose.** YNGVE DALSTRÖM (*Arkiv. Kem. Min. Geol.*, 1913, 4, No. 30, 1—14).—The source of ultraviolet light was an arc burning between carbon or iron electrodes. The apparatus was similar to that used by Euler and

Ohlson (A., 1911, i, 524), the temperature being 70°. The progress of any reaction taking place was followed by observing the change in rotation of the solutions used, and by titrating any acid formed with standard barium hydroxide solution.

The action of the light of short wave-length produced by the above-mentioned arcs consists, in the first instance, in the formation of an organic acid, which then brings about the hydrolysis of the remaining sucrose. Any direct action of the ultraviolet light on the hydrolysis can only be very small.

T. S. P.

**Action of Reducing Agents on the Chloraloses.** MAURICE JASRIOT and ANDRÉ KLING (*Compt. rend.*, 1913, 156, 1380—1382).— $\alpha$ - and  $\beta$ -Chloralose and galactochloralose are reduced in aqueous solution by aluminium activated with mercury, one of the chlorine atoms being replaced by hydrogen, and the products obtained are the same as in the action of ammonia on the chloraloses (compare A., 1911, 524, 525). In alkaline solution, sodium amalgam removes a second atom of chlorine, and from  $\alpha$ -chloralose a compound,  $C_6H_{11}O_6 \cdot CH_2Cl$ , m. p. 168°, is obtained.  $\beta$ -Chloralose yields a similar compound, m. p. 166°, giving a *dibenzoyl* derivative, needles, m. p. 149°, and on oxidation with nitric acid it yields a non-crystalline substance giving with hydrazine hydrate a compound,  $C_7H_7O_5Cl \cdot N_2H_4$ , white needles, m. p. 170°.

Sodium in liquid ammonia removes the third chlorine atom from the chloralose, but the product of the action could not be crystallised, the action seeming to lead to the destruction of the chloralose nucleus.

W. G.

#### Pseudo-crystals of Starch and Crystals of Dextrose.

GIOVANNI MALFITANO and (Mlle.) A. N. MOSCHKOV (*Compt. rend.*, 1913, 156, 1412—1415. Compare A., 1910, i, 301, 817).—The so-called crystals of starch, when examined microscopically, although resembling crystals of dextrose fairly closely, are found not to have a true crystalline form. These particles of starch have not the polyhedral form, neither do they exhibit the phenomenon of birefringence.

W. G.

**The Molecular Size of Dextrin- $\beta$ .** WILHELM BILTZ and WILHELM TRUTH (*Ber.*, 1913, 46, 1377—1380. Compare Pringheim and Langhans, A., 1912, i, 832).—The osmotic pressures exerted by dilute solutions of dextrin  $\beta$  in a cell composed of collodion impregnated with copper ferrocyanide have been measured directly, and the calculated molecular weights plotted against concentration. By extrapolation for infinite dilution, the value  $950 \pm 50$  is obtained, which confirms the expectation that dextrin- $\beta$  is a hexa-amylose. The fact that the curve rises rapidly with increasing concentration is not due so much to association as to the time required to reach equilibrium, for higher pressures and therefore lower molecular weights are obtained when the water column is allowed to sink to position than when it is made to rise. The method is being described



in another place. The results obtained for similar substances compare favourably with the values obtained by cryoscopic and other means.

J. C. W.

**Cellulose.** EDWARD G. PARKER (*J. Physical Chem.*, 1913, 17, 219—229).—Lange's method of estimating cellulose by hydrolysing the non-celluloses with potassium hydroxide, and the various modifications of it which have been proposed, give untrustworthy results, as the yield of normal cellulose varies with slight variations in the time of boiling, concentration of alkali, and temperature. By heating in a paraffin bath at 130—140° under reflux, after a certain interval of time the yield of normal cellulose from absorbent cotton became constant. The time required for the hydrolysis of the non-celluloses was less with dilute potassium hydroxide within the limits used, a 1 or 2% solution requiring three hours and a 20% solution fifteen hours. It is suggested that the increased evolution of steam from the dilute solutions carried the non-celluloses more rapidly into suspension where the alkali could act on them.

The author's sample of cotton wool contained approximately 92—93% of normal cellulose, 4—5% of soluble cellulose, and 3.25% of water.

Samples of oxycellulose prepared by the action of hydrochloric acid and potassium chlorate and of cellulose reprecipitated from cupraammonium solution contain a much higher proportion of matter soluble in potassium hydroxide. It is suggested that the soluble part of cotton wool consists of oxy- and hydro-cellulose and that cotton reprecipitated from Schweitzer's reagent consists largely of oxycellulose.

R. J. C.

**Esters of Cellulose with Benzoic Acid and their Derivatives.** G. J. BRIGGS (*Zeitsch. angew. Chem.*, 1913, 26, 255—256).—Hauser and Muschner have stated (this vol., i, 363) that they were unable to prepare the dibenzoate and tetrabenzoate described by Cross and Bevan. The author gives in detail the methods which were employed in the preparation of these derivatives of cellulose. Both esters are obtained by treating alkali cellulose with a 5—10% solution of benzoyl chloride in benzene, and are separated, first by treating the crude product with chloroform or glacial acetic acid in which the tetrabenzoate dissolves, and then by treating the residue with a cupraammonium solution which removes the unattacked cellulose.

W. H. G.

**Oxycellulose.** R. OERTEL (*Zeitsch. angew. Chem.*, 1913, 26, 246—250).—The oxycelluloses prepared by the methods of Witz, Nastukoff, Vignon, or Faber and Tollens are not simple substances. An oxycellulose having properties differing from those already known and described in the literature is obtained by passing an electric current between platinum electrodes and through a solution of potassium chloride containing cellulose in suspension. Under this treatment a large proportion of the cellulose is decomposed and passes into solution, but if the electrolysis is not carried too far, a product

is obtained which is soluble in a 10% solution of sodium hydroxide and has a copper value of 21.0—29.6 according to the extent of the electrolysis, the reducing power becoming greater as the treatment is prolonged. If the electrolysis be carried sufficiently far, the product obtained dissolves in water, forming a stable, colloidal solution, and has a copper value as high as 39.5.

The oxycellulose prepared by the electrolytic method is rapidly destroyed by a hot solution of sodium hydroxide, and when dissolved in a cuprammonium solution gives a very limpid solution. It is converted by sulphuric acid into dextrose, but the yield is not so high as in the case of cellulose, for whereas 100 parts of the latter yield 111 parts of dextrose, 100 parts of oxycellulose yield only 100 parts of dextrose. Oxycellulose when acetylated, using zinc chloride as catalyst, yields an acetate, part of which is soluble in acetone and has  $[\alpha]_D - 17^\circ$ , and part in chloroform ( $[\alpha]_D - 19^\circ$  to  $-20^\circ$ ); the proportion of acetyl radicle present in the product is not so high as in cellulose triacetate.

The yield of cellobiose acetate from oxycellulose is also not so great as from cellulose.

W. H. G.

**Formation of Humic Substances by the Action of Polypeptides on Sugars.** LOUIS C. MAILLARD (*Compt. rend.*, 913, 156, 1159—1160. Compare A., 1912, i, 13, 169; this vol., 165).—Glycylglycine like glycine itself readily reacts with xylose and dextrose in the presence of water, with the evolution of carbon dioxide and formation of brown humus-like substances, which are soluble in boiling water and dilute acids, but partly soluble in ammonia and potassium hydroxide, from which solutions they are precipitated on neutralisation. Three samples of commercial cepones behaved similarly with the sugars.

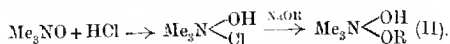
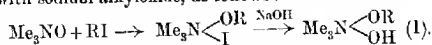
W. G.

**Some Tetramethylammonium Compounds.** JAROSLAV MILHAER (*J. pr. Chem.*, 1913, [ii], 87, 397—403). The following tetramethylammonium salts are described: *perchlorate*, white crystals solubility in cold water 1:126:100; *permanganate*, purple-red, tetragonal crystals, which readily decompose on exposure to moist air, and explode violently when heated. The *dithionate*, prepared by the interaction of the sulphate and barium dithionate in aqueous solution, forms lustrous, transparent, colourless cubes and octahedra. The *thiocyanate* crystallises in white, felted needles, the *stannichloride* in rhizic, microscopic octahedra, and the *stannibromide* in pale yellow, microscopic octahedra. The *borate*,  $(\text{NMe}_4)_2\text{B}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ , forms strongly refractive, transparent crystals, probably belonging to the triclinic system. The *sulphide* and *fluoride* could not be obtained in a pure condition.

F. B.

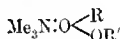
**Non-equivalence of the Five Valencies of Nitrogen.** JAKOB MEISENHEIMER (*Annalen*, 1913, 397, 273—300). The author's explanation of the existence of amine-oxides in enantiomorphous configurations (A., 1912, i, 25) tacitly assumes the non-equivalence of the five valencies of the nitrogen atom. Many facts can be quoted in support

of the assumption, but it has now been definitely proved. Trimethylamine oxide reacts additively with an alkyl iodide, and its hydrochloride reacts with sodium alkylxide, as follows:



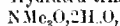
The position of the halogen atom in the ammonium salt is occupied by OH in substance (I) and by OR in substance (II). Several such pairs of isomerides have been prepared, and in every case the two substances are fundamentally different. The substances have not been isolated in the solid state, but by the evaporation of its aqueous solution, substance (I) decomposes quantitatively into trimethylamine, an aldehyde, and water, whereas substance (II) yields trimethylamine oxide and the alcohol R·OH. Pairs of isomerides of the types  $\text{Me}_3\text{N} \begin{smallmatrix} \text{OR} \\ \text{OR}' \end{smallmatrix}$  and  $\text{Me}_3\text{N} \begin{smallmatrix} \text{OR}' \\ \text{OR} \end{smallmatrix}$  have also been obtained; the evaporation of their solutions yields trimethylamine, an alcohol, and one aldehyde, the aldehyde always being that corresponding with the alkyl group of the alkoxy group not attached to the unique "fifth" valency of the quinquivalent nitrogen atom. Consequently, the two alkoxy-groups are not attached to the nitrogen atom in the same manner.

The author discusses the constitutions of the isomerides  $\text{Me}_3\text{N} \begin{smallmatrix} \text{OR} \\ \text{OR}' \end{smallmatrix}$  and  $\text{Me}_3\text{N} \begin{smallmatrix} \text{OR}' \\ \text{OR} \end{smallmatrix}$ , and gives reasons for rejecting formulæ:



and  $\text{Me}_3\text{N} \begin{smallmatrix} \text{R}' \\ \text{OR} \end{smallmatrix}$ ,  $[\text{Me}_3\text{NO}] \dots \text{R} \cdot \text{OR}'$  and  $[\text{Me}_3\text{NO}] \dots \text{R}' \cdot \text{OR}$ , and  $[\text{Me}_3\text{N} \dots \text{OR}] \text{OR}'$  and  $[\text{Me}_3\text{N} \dots \text{OR}'] \text{OR}$ , based on the oxonium, oxonium-ammonium, and (Werner's) ammonium theories respectively. A modification of the last theory is adopted. In Werner's formula of ammonium chloride, the nitrogen atom still remains in a sense tervalent; the four hydrogen atoms are attached to the nitrogen atom each by an amount of affinity less than that corresponding with a principal valency, so that the group NH<sub>4</sub> has an amount of residual affinity whereby it functions as a univalent group and is attached to the acid radicle. Objections can be raised against this view (compare Moore and Winnill, T., 1912, 101, 1673). The author is of opinion that in ammonium compounds the nitrogen is quinquivalent, all five atoms or groups being attached to it by principal valencies, four in an inner, the fifth in an outer, zone; the atom or group in the outer zone is not attached in any definite position, and therefore exerts no influence on the asymmetry of the molecule. The author's pairs of isomerides are consequently represented by the formulæ:  $[\text{Me}_3\text{N} \cdot \text{OR}] \cdot \text{OR}'$  and  $[\text{Me}_3\text{N} \cdot \text{OR}'] \cdot \text{OR}$ , which satisfactorily represent their behaviour.

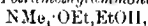
[With KURT BRATRING.]—Hydrated trimethylamine oxide,



prepared best by Dunstan and Goulding's method (T., 1899, 75, 1005), can be dehydrated by heating under 10—12 mm. at a tempera-

ture not exceeding  $150^{\circ}$  until the greater part of the water has been expelled; the temperature is then raised to  $190$ — $200^{\circ}$ , when *trimethylamine oxide*,  $\text{NMe}_3\text{O}$ , sublimes in colourless needles, m. p.  $208^{\circ}$ , which are extremely hygroscopic. By boiling for three-quarters of an hour with ethyl iodide in ethyl alcohol or with propyl iodide in propyl alcohol, the anhydrous oxide is readily converted into additive compounds,  $\text{OEt}\cdot\text{NMe}_3\text{I}$ , m. p.  $123$ — $125^{\circ}$ , and  $\text{OPr}\cdot\text{NMe}_3\text{I}$ , m. p.  $145$ — $147^{\circ}$ , respectively, both colourless, crystalline substances. By treating a dilute aqueous solution of methoxytrimethylammonium iodide with silver oxide and subsequently with cold hydrochloric acid and evaporating, *methoxytrimethylammonium chloride*,  $\text{OMe}\cdot\text{NMe}_3\text{Cl}$ , is obtained, but the evaporation of an alcoholic solution of the methoxytrimethylammonium hydroxide without the addition of hydrochloric acid results in the formation of trimethylamine (isolated as the platinumchloride) and formaldehyde (isolated as the *p*-nitrophenylhydrazone). Similar results are obtained by the evaporation of alcoholic solutions of ethoxytrimethylammonium hydroxide and propoxytrimethylammonium hydroxide, acetaldehyde and propionaldehyde, respectively, being formed. By treating trimethylamine oxide hydrochloride, dissolved in the necessary alcohol, with the calculated amount of sodium methoxide, ethoxide, or propoxide, *hydroxytrimethylammonium methoxide*, *ethoxide*, and *propoxide* respectively are produced,  $\text{OH}\cdot\text{NMe}_3\cdot\text{OR}$ . By evaporation of their alcoholic solutions, these substances yield no trimethylamine, and only a trace of an aldehyde; the residue in all three cases is converted into trimethylamine oxide hydrochloride by alcoholic hydrogen chloride.

[With J. DOVONOW.]—*Tetramethylammonium ethoxide*,



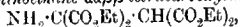
hygroscopic crystals, is obtained by treating tetramethylammonium chloride in anhydrous alcohol with the calculated amount of sodium ethoxide, adding ether, and removing the sodium chloride by filtration and the solvent by evaporation in a vacuum at  $40^{\circ}$ . *Alkyloxytrimethylammonium alkyloxides*,  $[\text{NMe}_3\cdot\text{OR}]\cdot\text{OR}'$ , are obtained in alcoholic solution by treating alkyloxytrimethylammonium iodides with alcoholic sodium alkyloxides. The substances have not been isolated, but the products of their decomposition by the evaporation of their alcoholic solutions in a current of nitrogen have been examined. *Methoxytrimethylammonium ethoxide* and *methoxytrimethylammonium propoxide* each yield formaldehyde, *ethoxytrimethylammonium methoxide* and *ethoxytrimethylammonium propoxide* each yield acetaldehyde, whilst *propoxytrimethylammonium methoxide* yields propionaldehyde.

[By the AUTHOR.] It is probable that phosphonium compounds have a constitution similar to that of ammonium compounds suggested by the author; the existence of phosphorus pentachloride is not evidence against the probability, since the equivalence of the five chlorine atoms has not been proved. The additive compound of phosphenyl chloride and bromine, therefore, should be different from that of phosphenyl bromide and chlorine, the two substances having the constitutions  $[\text{PPhCl}_2\text{Br}]\text{Br}$  and  $[\text{PPhBr}_2\text{Cl}]\text{Cl}$  respectively. Experiment shows, however, that the two substances are identical.

C. S.

**Action of Ethylene Dibromide, Methylene Iodide, and Iodine on Ethyl Aminocrotonate.** ERICH BENARY (*Ber.*, 1913, 46, 1375—1377).—Unlike chloroacetyl chloride, ethylene dibromide and methylene iodide do not form pyrrole derivatives on condensation with ethyl aminocrotonate in presence of pyridine, but they give rise to ethyl dihydrocollidinedicarboxylate and ethyl lntidinedicarboxylate respectively. When iodine is added to the sodium compound of ethylaminocrotonate in ether, *ethyl iodoaminocrotonate*,  $\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , is obtained in soft leaflets, m. p.  $83-84^\circ$ , which are hydrolysed by dilute sulphuric acid to ethyl  $\alpha$ -iodoacetoacetate (compare ethyl bromoaminocrotonate, Behrend, A., 1900, i, 210): J. C. W.

**The Reaction Products of Ammonia on Ethyl Dicarbintetracarboxylate.** ROLAND SCHOLL, KARL HOLDERMANN, and ARMIN LANGER (*Monatsh.*, 1913, 34, 623—629).—Ethyl dicarbintetracarboxylate [ethyl ethylenetetracarboxylate] is best prepared by the method of Blank and Samson (A., 1899, i, 484). It reacts slowly with a saturated alcoholic solution of ammonia at the ordinary temperature, producing *ethyl  $\alpha$ -aminoethane- $\alpha\beta\beta$ -tetracarboxylate*,



as an additive product. This is an oily liquid which dissociates into its two components when distilled under reduced pressure and also regenerates ethyl ethylenetetracarboxylate when treated with nitrous acid. The stability of the amino-acid towards acid and alkali is believed to be incompatible with the alternative structure suggested by the two reactions just cited (compare Meister, A., 1888, 675).

If a bomb tube containing a mixture of liquid ammonia and ethyl ethylenetetracarboxylate is kept sealed at the ordinary temperature for sixty hours, tablet or prismatic crystals of  *$\alpha$ -aminoethane- $\alpha\beta\beta$ -tetracarboxylamide*,  $\text{NH}_2\cdot\text{C}(\text{CO}\cdot\text{NH}_2)_2\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)_2$ , separate. This substance is unstable and smells of ammonia; it is decomposed by water, and when heated alone, gradually decomposes with final carbonisation. D. F. T.

**The Course of the Action of Ammonia on Ethyl Dicarbintetracarboxylate.** ERNST PHILIPPI and ALFRED UHL (*Monatsh.*, 1913, 34, 717—731. Compare preceding abstract).—The paper opens with a discussion of various theories as to the mechanism of amide formation.

Carefully dried ammonia was passed for twenty minutes, after all sign of heat evolution had disappeared, into a suspension of ethyl ethylenetetracarboxylate (ethyl dicarbintetracarboxylate) in absolute alcohol, and the resultant solution kept for three months; a yellowish-white, crystalline crust separated. The alcoholic mother liquid contained a little unaltered ester together with an oily additive compound of molecular proportions of ammonia and ester; *platinichloride*, yellow, microscopic, columnar crystals. The additive compound is believed to be *ethyl  $\alpha$ -aminoethane- $\alpha\beta\beta$ -tetracarboxylate*, the presence of the carboxyl groups having so increased the activity of the ethylenic linking of the original ester as to cause addition at this position; such addition of ammonia has been observed at the double bond of several ethylenic esters. When boiled for several hours with 2*N*-hydrochloric

acid, carbon dioxide is set free, leaving the hydrochloride of aspartic acid. A solution of the additive compound in hydrochloric acid when treated with nitrous acid regenerates ethyl ethylenetetracarboxylate; this behaviour is explained by the primary formation of the expected hydroxy-compound, which immediately passes into the ethylenic ester with loss of a molecule of water. The solid crust obtained in the initial experiment consisted of  $\alpha$ -aminoethane- $\alpha\beta\beta$ -tetracarboxylamide, a hygroscopic, unstable substance which decomposes on moderate heating. Altogether 89.6% of the original ester could be accounted for in the products.

D. F. T.

**Internally Complex Metallic Salts of Derivatives of Oxalic Acid and of Triformaldoxime.** KARL A. HOFMANN and UDO EHRLARDT (*Ber.*, 1913, 46, 1457—1466).—Various amido-derivatives of oxalic acid have been examined in connexion with the power of formation of internally complex salts, because their structure is such as to suggest an easy formation of a ring composed of five atoms. It is discovered that the stability of the complex salt depends on the number of amido- or imido-groups present, for, of the substances examined, oxamic acid shows least tendency, whilst oxalhydrazide shows the greatest tendency to formation of complex salts. This increase in tendency to form complex salts caused by the increase in supplementary valencies due to the nitrogen atoms accords well with the views of Ley (A., 1905, i, 175) as to the structure of such salts.

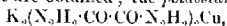
As criteria for the occurrence of internally complex salts were accepted an abnormal colour (usually intense), and stability towards alkali and acetic acid. The salts were prepared in each case in alkaline solution, and caused to crystallise by the addition of methyl alcohol.

Oxamic acid under the above conditions gave no complex salt with a nickel, iron, or manganese salt, but with copper acetate and concentrated potassium hydroxide solution, bluish-violet needles of a *potassium-copper* salt,  $K_2(NH \cdot CO \cdot CO_2)_2Cu$ , were obtained, which are decomposed by excessive alkali or by pure water, yielding copper oxide.

Oxamide gave no compound with iron or manganese, but yielded a *potassium-copper* salt,  $K_2(NH \cdot CO \cdot CO \cdot NH)_2Cu \cdot 1\frac{1}{2}H_2O$ , reddish-violet needles, soluble in alkali to a violet-blue solution, which slowly decomposes, and a *potassium-nickel* salt,  $K_2(NH \cdot CO \cdot CO \cdot NH)_2Ni$ , bright yellow plates soluble in dilute hydroxide solution to an unstable golden-yellow solution.

Oxalaminohydrazide yielded a *potassium-copper* salt, violet-red needles,  $K_2(NH \cdot NH \cdot CO \cdot CO \cdot NH)_2Cu \cdot 2H_2O$ , which, when moist, undergoes gradual decomposition into a basic copper oxamate, and a *potassium-nickel* salt,  $K_2(NH \cdot NH \cdot CO \cdot CO \cdot NH)_2Ni$ , golden-yellow rods, which dissolve in water to a reddish-yellow solution without decomposition (compare Kerp and Unger, A., 1897, i, 270; Schiff, A., 1902, i, 85).

Oxalhydrazide in strong alkali solution with nickel acetate gives a violet solution, but on crystallisation yellow, hexagonal prisms of a more complex product are obtained; the *potassium-copper* salt,



forms bright brown needles, decomp.  $270^\circ$ , soluble in water to a greenish-yellow colour.

Hydroxyloxamide gives a *sodium-copper* salt,  
 $\text{Na}_4(\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NO})_2\text{Cu}\cdot 4\text{H}_2\text{O}$ ,  
 reddish-violet needles, and a *sodium-nickel* salt,  
 $\text{Na}_4(\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NO})_2\text{Ni}\cdot 2\text{H}_2\text{O}$ ,  
 orange-yellow, hexagonal prisms, which decomposes about  $280^\circ$ . From the composition of those two salts the authors are of the opinion that the salts are derived by displacement of hydroxylic hydrogen, and that under the influence of the alkali used in the process of preparation the  $-\text{CO}\cdot\text{NH}_2$  group undergoes a preceding change into the structure  $-\text{C}(\text{NH})\text{OH}$ . With bivalent and trivalent iron, also, hydroxyloxamide gives yellowish-red alkaline solutions.

Oxalodihydroxamic acid gives a *potassium-copper* salt,  
 $\text{K}_3(\text{C}_4\text{N}_4\text{O}_8\text{H}_2)\text{Cu}$ ,  
 brownish-red needles, which decompose at  $180^\circ$ , and a *potassium-nickel* salt,  $\text{K}_3(\text{C}_4\text{N}_4\text{O}_8\text{H}_2)\text{Ni}\cdot \text{H}_2\text{O}$ , brownish-yellow needles. Cobalt and iron salts in the presence of excess of alkali give reddish-yellow solutions with oxalodihydroxamic acid.

Formaldoxime is known to give deep colorations with copper, iron and nickel solutions in the presence of potassium hydroxide (compare Dunstan, T., 1898, 73, 353), but complex salts have now been isolated for the first time. The colour of the solutions is so intense that manganese, iron, and nickel can be detected at a dilution of one part in a million; the solution of the manganous salt is yellow, but rapidly oxidises in the air to a *manganic* salt,  $(\text{CH}_2\cdot\text{NO})_3\text{Mn}\cdot 2\text{H}_2\text{O}$ , blackish brown, rectangular plates, which decompose above  $220^\circ$ , and give an intense reddish-brown solution in water. The almost colourless alkaline solution of the nickelous salt in a similar manner absorbs oxygen yielding a deep brown solution of the *sodium-nickelic* salt,

$\text{Na}_3(\text{CH}_2\cdot\text{NO})_6\text{Ni}$ ,  
 steel-blue, lustrous crystals, which decompose near  $225^\circ$ . The volume of oxygen absorbed in the two previous oxidations was in good accord with the theoretical. In a similar manner the yellowish-red alkaline solution of the ferrous salt undergoes gradual oxidation to the deep violet-red solution of the *sodium-ferric* salt, which is better obtained by using a ferric salt directly; the *sodium-ferric* salt,

$\text{Na}_3(\text{CH}_2\cdot\text{NO})_6\text{Fe}\cdot \text{H}_2\text{O}$ ,  
 forms blue, hexagonal plates, which decompose near  $195^\circ$ . The structure of these salts is believed to be analogous to that of the internally complex salts of the dioximes.  
 D. F. T.

**Synthesis of Parabanic and Substituted Parabanic Acids**  
 HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1913, 46, 1387—1404).—The authors have effected the synthesis of parabanic and substituted parabanic acids by the action of oxalyl chloride on carbamide and substituted carbamides in ethereal or, more rarely, acetic anhydride solution. Reaction generally takes place smoothly, and the yields, particularly with doubly-substituted carbamides, are excellent. In the case of parabanic acid itself, and, possibly, of dimethylparabanic acid however, the older methods are simpler and cheaper.

Parabanic acid was obtained in small yield by the action of a boiling ethereal solution of oxalyl chloride on carbamide, and was identical

by conversion into its silver salt. Oxalyldicarbamide,  $C_4H_6O_4N_4$ , m. p. 270—275° (decomp.), was isolated as by-product. Similar observations have been made by Bornwater (A., 1911, i, 617). Methylparabanic acid, m. p. 153—154°, b. p. 201—202°/13 mm., and oxalyldimethylcarbamide, m. p. 230—232° (decomp.), were similarly prepared from methylcarbamide. An attempt to prepare oxalyldimethylcarbamide by melting methylparabanic acid with methylcarbamide was unsuccessful. Boiling acetic anhydride converted methylparabanic acid into 3-acetyl-1-methylparabanic acid, m. p. 183—185°, which was also obtained by the action of oxalyl chloride on acetylmethylcarbamide. Cold aqueous hydrochloric acid was without action on it, whilst the hot reagent caused great decomposition. Saturation of an absolute alcoholic suspension of it with hydrogen chloride brought about the elimination of the acetyl group, methylparabanic acid being formed in almost quantitative yield.

Dimethylparabanic acid, leaflets, m. p. 154°, b. p. 148—150°/13 mm., was obtained in 70% yield from *s*-dimethylcarbamide and oxalyl chloride, and also from *s*-dimethylcarbamide and ethyl chloropropionate.

*Dimethylcarbamide hydrochloride*, needles, m. p. 124°, was obtained by saturating a solution of *s*-dimethylcarbamide in ethyl acetate with hydrogen chloride. *Methylcarbamide hydrochloride*, prepared similarly, is very hygroscopic. It has m. p. about 85—87° after softening at about 70°, and evolves hydrogen chloride at about 125°.

Ethylparabanic acid, m. p. 127—128°, and *oxalyldiethylcarbamide*, needles, m. p. 220—222° (decomp.), were obtained from ethylcarbamide and oxalyl chloride. The properties of the first-named substance differ from those of the ethylparabanic acid described by Andreass (A., 1898, i, 243).

9-Ethyluric acid glycol (A., 1910, i, 526) was oxidised by potassium dichromate and sulphuric acid to ethylparabanic acid. An attempt was also made to degrade the former substance to the latter in the manner adopted for 7:9-dimethyluric acid (Biltz and Krebs, A., 1910, i, 521). An aqueous solution of the glycol was converted by heat into 5-hydroxy-3-ethylhydantoincarbamide, which was transformed into 3-ethylcaffolide and ammonium chloride when treated with hydrochloric acid and subsequently evaporated to dryness. When an aqueous solution of 3-ethylcaffolide was boiled, 5-hydroxy-3-ethylhydantoinamide was formed, which, when oxidised, yielded ethylparabanic acid. The intermediate products could not be obtained in the crystalline state, but the course of the degradation can be deduced from the final product and from the isolation of the by-products expected in the various stages.

Diethylparabanic acid, needles, m. p. 49—51°, b. p. 138—140°/13 mm., was obtained in 78% yield from *s*-diethylcarbamide and oxalyl chloride, and was identical with the product obtained by the degradation of 7:9-diethyluric acid glycol (A., 1911, i, 693). Diethylthioparabanic acid had h. p. 148—150°/13 mm.

Phenylparabanic acid, m. p. 213—214° after softening at 208° [Stoientum (A., 1885, 1196) gives m. p. 208°], diphenylparabanic acid, m. p. 202° after previous softening, *benzylparabanic acid*, m. p.



167—169°, and *pp-bisbromophenylparabanic acid*,  $C_{12}H_8O_3N_2Br_2$ , were prepared in an analogous manner.

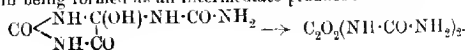
Thiocarbamide reacted vigorously with oxalyl chloride at first, but, even in the presence of a considerable excess of the latter, was not completely converted into *thioparabanic acid*. By repeated crystallisation from ethyl acetate, the latter was obtained in yellowish-red, indistinct crystals, m. p. 215—220° (decomp.), and was further identified by conversion into the *silver* salt,  $C_3O_2N_2SAg_2$ , and transformation of the latter into 1:3-dimethylthioparabanic acid, m. p. 113—115° [Andreasch (A., 1881, 897) gives 112·5°], by means of methyl iodide. When desulphurised by means of hydrochloric or nitric acids, this substance yielded dimethylparabanic acid. Dimethylthioparabanic acid was also prepared by the action of oxalyl chloride on dimethylthiocarbamide, and then had m. p. 113—115°, after softening at 110°, b. p. 153—155°/13 mm.

The authors have also examined the "thioparabanic acid" obtained by Michael (A., 1894, i, 164) by the condensation of thiocarbamide with ethyl oxalate in the presence of sodium ethoxide. They find that it softens at 165°, and has m. p. 173—175° (decomp.). The fusion separates into two layers, the upper one of which begins to distil at about 199°. Since also this substance slowly yields a precipitate with calcium chloride and ammonia, even at the ordinary temperature, the authors are led to the conclusion that it is an additive compound of thiocarbamide and ethyl oxalate (compare Nencki, A., 1874, 981).

Ethylthioparabanic acid was obtained in small yield from ethylthiocarbamide and oxalyl chloride, the loss being chiefly attributable to the difficulty of separating the acid from unchanged ethylthiocarbamide by crystallisation. The observed m. p., 65—69°, is sufficiently close to that found by Andreasch (66°, *loc. cit.*) to prove the identity of the two products. Desulphurisation by means of a boiling alcoholic solution of silver nitrate converted ethylthioparabanic acid into ethylparabanic acid, m. p. 127—128°.

Diphenylthioparabanic acid, pale yellow needles, m. p. 228—230°, was obtained in 94% yield from *s*-diphenylcarbamide and ethereal oxalyl chloride. H. W.

**Oxalyldicarbamide.** HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1913, 46, 1404—1417. Compare preceding abstract, and also Bornwater, A., 1911, i, 617).—When an ethereal solution of oxalyl chloride reacts with finely-powdered carbamide, parabanic acid is formed together with a substance characterised by its very sparing solubility in ordinary solvents, to which the constitution  $C_3O_2(NH\cdot CO\cdot NH_2)_2$  is ascribed. This latter substance differs from the oxalyldicarbamide prepared by Grimaux by the fusion of a mixture of parabanic acid and carbamide (A., 1880, 105) in that it gives no biuret reaction, whereas Grimaux's compound yields a faint violet coloration with potassium hydroxide and copper sulphate. Further, oxalyldicarbamide may also be obtained by the oxidation of allantoin in acid solution, 5-hydroxy allantoin being formed as an intermediate product:



The authors have made a comparative critical examination of these three products, and are led to the conclusion that they are probably identical. The coloration given by Grimaux's compound with potassium hydroxide and copper sulphate is probably due to the presence of some impurity, the nature of which could not be established, but which is neither biuret, oxamide, allantoxanic acid nor allantoxidine. Certain differences, however, remain unexplained. Thus, oxalyldicarbamide, when acted on by hydriodic acid, yields hydantoin together with other products, whilst, in similar circumstances, Grimaux's compound gives a substance,  $C_4H_5O_3N_3$ , in small quantity. Also, potassium hydroxide transforms all three compounds mainly into oxaluric acid and oxalic acid, but differences are found among the by-products of the action.

Ponomarev's observation (A., 1885, 760) that concentrated potassium hydroxide converts Grimaux's compound into potassium allantoxanate is probably incorrect.

Oxalyldicarbamide was obtained by the oxidation of an aqueous solution of allantoin and sodium acetate by means of ammonium persulphate or by potassium permanganate in dilute acetic acid solution. A portion of the allantoin remained unattacked even when an excess of the oxidising agent was used, whilst, also, oxaluric acid was formed. The latter was isolated in the form of its ammonium salt, needles, decomposing at  $243-245^\circ$ , from which the free acid and also the silver salt were obtained.

Grimaux's compound was obtained by heating a mixture of parabanic acid and carbamide and purified by extraction with boiling water. Such preparations yielded with potassium hydroxide and copper sulphate violet colorations of varying intensity. By repeated solution of the product in concentrated sulphuric acid, re-precipitation by means of water, and subsequent repeated extraction with boiling water, substances were obtained which gave only a very faint violet coloration, but the impurity could not thus be completely removed.

All three preparations evolved ammonia at the ordinary temperature when treated with potassium hydroxide (D 1.1-1.4). Under similar conditions oxalyldimethylcarbamide evolved only methylamine, whilst oxalyldiethylcarbamide gave ethylamine. These substances must therefore have the formulae  $C_2O_2(NH \cdot CO \cdot NHMe)_2$  and  $C_2O_2(NH \cdot CO \cdot NHEt)_2$  respectively.

When treated with potassium hydroxide under varying conditions, neither of the compounds yielded potassium allantoxanate. Specimens of oxalyldicarbamide, prepared from oxalyl chloride or from allantoin, yielded carbon dioxide, potassium oxalate, and potassium oxalurate. Grimaux's compound yielded mainly potassium oxalurate; sometimes, also, a potassium salt which crystallised in short prisms, became somewhat discoloured at  $280^\circ$ , but was not greatly decomposed at  $360^\circ$ . This salt was probably derived from the impurity which yields the violet coloration, since it gave a distinct violet colour with potassium hydroxide and copper sulphate. In one experiment a second potassium salt, prisms, was obtained, which, with hydrochloric acid, yielded the free acid. The latter was sparingly soluble in water, darkened from  $275^\circ$  onwards, but showed no decomposition point below  $360^\circ$ .

The three compounds were very stable towards acid, and no differences were observed in their behaviour in this respect. Oxalic acid, but no parabanic acid, was obtained from each by the action of boiling fuming nitric acid. Concentrated hydriodic acid (D 1.5) converted Grimaux's compound into oxalic acid. The formation of methyl- and ethyl-parabanic acids by the action of boiling glacial acetic acid on dimethyl- and diethyl-oxalyldicarbamide (compare previous abstract) must be attributed to the formation of the glyoxalone ring during the course of the action, since oxaluric acid itself is partly transformed into parabanic acid by prolonged treatment with boiling glacial acetic acid.

Hydantoin, m. p. 215—217°, and ammonium iodide were obtained by the action of fuming hydriodic acid (D 1.96) at 130—140° on oxalyldicarbamide obtained from oxalyl chloride or from allantoin. Under similar treatment, Grimaux's compound yielded a substance,  $C_4H_5O_3N_3$ , leaflets, m. p. 270—273° (decomp.), which behaved as a monobasic acid. The ammonium salt formed needles, which decomposed at 270—273°. The silver salt,  $C_4H_4O_3N_3Ag$ , was analysed, and appeared to contain a certain amount of silver united to nitrogen.

H. W.

**Oxalyl Chloride. V. Oxalyl Bromide and Attempts to Prepare Dicarboxic Dioxide.** HERMANN STAUDINGER and E. ANTONES (*Ber.*, 1913, 46, 1426—1437. Compare A., 1912, i, 567).—The authors have prepared oxalyl bromide, which they find to be more readily decomposed by heat and more reactive than the corresponding chloride. In the hope of isolating dicarboxic dioxide,  $CO:CO$ , they have investigated the action of metals on it. Ready interaction occurs with both zinc and mercury, but in each case carbon monoxide is evolved, so that dicarboxic dioxide is probably incapable of existence at the ordinary temperature. With potassium, or the liquid alloy of sodium and potassium, an explosive product is formed, to which the authors attribute the composition  $OK \cdot C \cdot C \cdot OK$ .

Phosphorus pentabromide (2 mols.) reacts slowly with anhydrous oxalic acid (1 mol.). If the mixture is warmed, oxalyl bromide is not obtained, nor is the process improved by mixing the materials with sand. If, however, phosphoryl bromide is mixed with phosphorus pentabromide, the dried oxalic acid added, and the mixture maintained at 50° during one day and subsequently distilled, small quantities of oxalyl bromide are obtained. A better method consists in the treatment of well-cooled oxalyl chloride with hydrogen bromide (compare this vol., i, 616), when oxalyl bromide is obtained in 85% yield. It is a greenish-yellow liquid, b. p. 102—103°/720 mm., 16—17°/10 mm., m. p. —19.5°.

A boiling 20% ethereal solution of oxalyl chloride does not react with zinc even after addition of iodine, mercuric chloride, or a trace of water. In ethyl acetate solution, reaction occurs if the zinc has been activated by means of diphenylchloroacetyl chloride. Carbon monoxide is then formed. Mercury, sodium, silver, or magnesium turnings do not react with oxalyl chloride, but a brown precipitate is obtained with magnesium powder in the presence of ether, investigation of

which is incomplete. The vapour of oxalyl chloride is practically completely decomposed by silver at  $200^{\circ}$ , carbon monoxide being formed. With zinc practically no action occurs.

Oxalyl bromide, on the other hand, is readily decomposed by zinc or mercury at the ordinary temperature, carbon monoxide being formed. Mercurous bromide has no action on it at the ordinary temperature or at  $100^{\circ}$ . Sodium potassium amalgam reacts with oxalyl bromide without marked development of heat or alteration in appearance. The product, however, explodes violently when subjected to vibration. Attempts to cause potassium to react with oxalyl bromide vapour at  $130^{\circ}$  or in xylene solution were unsuccessful.

Oxalyl bromide gradually becomes pale reddish-brown when preserved, owing to separation of bromine, decomposition being catalysed by light. At  $100^{\circ}$  it is stable, but at  $150$ – $200^{\circ}$  is decomposed into carbon monoxide, bromine, and carbonyl bromide. Oxalyl chloride, on the other hand, could be heated during eighteen hours at  $200^{\circ}$  without noticeable decomposition occurring; at  $340^{\circ}$  it is completely decomposed during seventy hours into carbon monoxide and carbonyl chloride.

Oxalyl bromide reacts readily with benzaldehyde in light petroleum solution, forming a white additive *product*, m. p.  $131^{\circ}$ , with decomposition into benzaldehyde, benzylidene bromide, and carbon monoxide. Under similar conditions an additive *product* is slowly formed from oxalyl chloride, which, when rapidly heated, has m. p. about  $212^{\circ}$ , but loses carbon monoxide at a lower temperature.

Oxalyl bromide reacts more readily than the corresponding chloride with dimethylaniline, dimethylaminobenzoic acid, crystal-violet and tetramethyldiaminobenzil being formed.

Oxalyl iodide could not be isolated by the action of hydrogen iodide on oxalyl chloride. Even at  $-80^{\circ}$  only carbon monoxide and iodine were obtained. The latter substances were also produced quantitatively when a solution of oxalyl chloride in ethyl acetate was boiled with sodium iodide.

Unsuccessful attempts were also made to obtain diphenyloxalimino-bromide and iodide by the action of the requisite halogen acid on diphenyloxalimino-chloride,  $\text{NPh}_2\text{CCl} \cdot \text{CCl} \cdot \text{NPh}_2$ . The bromide could not be obtained from oxanilide by the action of phosphorus tri- or pentabromide.

H. W.

**An Ester of Hydrocobalticyanic Acid.** CHARLES E. BOLSER and L. B. RICHARDSON (*J. Amer. Chem. Soc.*, 1913, 35, 377–381).—By the action of ethyl iodide on silver cobalticyanide, suspended in alcohol, *ethyl dihydrogen cobalticyanide*,  $\text{EtH}_2\text{Co}(\text{CN})_5 \cdot \text{H}_2\text{O}$ , has been obtained as a yellowish-white solid which loses its water of crystallisation at a little over  $100^{\circ}$  and becomes blue. On the addition of silver nitrate to a solution of the ester, *disilver ethyl cobalticyanide* is produced as a white precipitate; a copper salt was also obtained. When the ester is treated with sodium hydroxide, ethylcarbamide is evolved, indicating that the ethyl group in some, if not all, of the molecules is attached to nitrogen.

An attempt was made to prepare the corresponding ester of hydroferrieyanic acid, but without success. E. G.

**Reaction of Nitroprussides with Acetone.** LIVIO CAMMI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 376-381).—In this reaction the production of the coloration is accompanied by the production of oximinacetone, for it is possible to isolate in impure form a coloured salt which yields this compound on treatment with alkali. Analogous results were obtained in the case of acetophenone, a coloured salt being obtained which yielded oximinacetophenone when treated with alkali. R. V. S.

**Maximum Yield of Amines by the Reduction of Alkyl Cyanides.** JITENDRA NATH RAKSHIT (*J. Amer. Chem. Soc.*, 1913, 35, 444-446).—A study of the conditions under which amines are produced by the reduction of nitriles has shown that the best yields can be obtained by the following modification of Ladenburg's method.

The nitrile (5 c.c.) is dissolved in 75 c.c. of alcohol and the solution is introduced in successive quantities of 5 c.c. into a flask containing 5 grams of sodium and attached to a reflux condenser. The mixture is heated at 50-60°. After 20 c.c. of the solution have entered the flask, 5 c.c. of alcohol are added, and the amine evolved on distillation is absorbed in dilute hydrochloric acid. When the whole of the nitrile solution has been introduced, alcohol is added until a layer remains above the solid sodium ethoxide in the flask. When the evolution of hydrogen ceases, the condenser is removed and the flask is connected directly to the absorption apparatus and heated as long as alkaline vapour is produced. If necessary, a further quantity of alcohol is added and the distillation continued. The acid solution is evaporated to dryness on the water-bath, and the amine hydrochloride extracted from the residue with a mixture of alcohol (15 c.c.) and ether (10 c.c.).

The results of experiments with acetonitrile, propionitrile, and butyronitrile show that the amines can be obtained by this method in nearly quantitative yield. E. G.

**Amylene-isonitroamineoxime and bisnitrosoisonitroamine.** GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 225-231. Compare A., 1911, i, 186).—Cryoscopic molecular weight determinations on the  $\beta$ -nitrosohydroxylamino- $\beta$ -methylbutan- $\gamma$ -oneoxime previously described, and on its sodium salt indicate that the compound is probably a bisnitrosoisonitroamine. Its formation is probably preceded, however, by that of an isonitroamineoxime which suffers rearrangement and polymerisation. In fact, the freshly prepared substance has m. p. 71°; later, or after recrystallisation, the m. p. is 82°, as formerly stated. Hence it is possible to proceed from oximes of the type  $\text{CX}\cdot\text{C}\cdot\text{N}\cdot\text{OH}$  to nitrosyl compounds,  $\text{CX}\cdot\text{CH}\cdot\text{NO}$ .

When the bisnitrosoisonitroamine is treated with sodium nitrite in aqueous solution, the bisnitroso-oxime,  $(\text{NO}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{NOH})_2$ , is

formed; the crystals at first melt at  $83^{\circ}$ , but later on, or after recrystallisation, the m. p. is  $140^{\circ}$ ; the substance is soluble in alkali hydroxides and in acids, and gives a blue coloration with diphenylamine and sulphuric acid.

The isonitroamineoxime previously described yields an ethyl ester,  $C_2H_5O_2N_3$ , m. p.  $119^{\circ}$ , which is prepared by means of the silver salt.

The isonitroamine of  $\beta$ -methylbutan- $\gamma$ -one,  $CM_2(N_3O_2H) \cdot COMe$ , is obtained by the action of hydrochloric acid on the sodium salt of the isonitroamineoxime, or by the action of nitrous acid on  $\beta$ -hydroxylamino- $\beta$ -methylbutan- $\gamma$ -one (previously described); it forms large, tabular crystals, m. p.  $62^{\circ}$ , and gives a blue coloration with diphenylamine and sulphuric acid. The substance has acid properties and is fairly stable, but when heated above its m. p. decomposes, leaving a partially crystalline residue, from which a substance crystallising in quadrangular tablets, m. p.  $99^{\circ}$ , can be isolated. R. V. S.

**Preparation of Fatty Acids and their Salts containing Arsenic and Phosphorus.** FELIX HEINEMANN (D.R.P. 257641).—When the unsaturated acids of the acetylene series are heated with the halogen derivatives of arsenic or phosphorus, they furnish acidic compounds having a high molecular weight and containing a halogen substituent in addition to phosphorus (or arsenic); they give rise to soluble alkali, and insoluble calcium and strontium salts.

The compound produced when stearolic acid and arsenic trichloride (1.5 parts) are heated together at  $140^{\circ}$  during six hours is obtained (by extraction with ether) as a viscous oil which gradually in part solidifies; it contains As=11% and chlorine 6–7%; the strontium salt, a flesh-coloured powder, contains 12% As; the calcium salt is also mentioned.

The compound from behenic acid and arsenic trichloride is a pale brown, viscous oil containing 8–9% As and 5–6% Cl; the strontium salt is a colourless powder.

When stearolic acid is heated with an equal quantity of phosphorus trichloride at  $140^{\circ}$  during fifteen hours, it furnishes two acidic compounds; one a viscous, brownish-yellow acid extractable with ether containing P=4–5% and Cl=8%; the other an orange-yellow resin insoluble in ether and containing P=15%. The analogous compound from behenic acid and phosphorus trichloride, and the strontium and calcium salts are also described, whilst the arsenic and phosphorus chlorides employed can be replaced by the corresponding bromides.

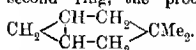
F. M. G. M.

**The Benzene Problem.** HANS VON LIEBIG (*J. pr. Chem.*, 1913, [ii], 87, 393–397. Compare A., 1912, i, 686).—A reply to Gebhard's criticism (this vol., i, 28).

F. B.

**3:3-Dimethyl-[0,1,3]-dicyclohexane. Its Synthesis and Behaviour on Catalytic Reduction.** NICOLAI D. ZELINSKI and A. E. USPENSKI (*Ber.*, 1913, 46, 1466–1474).—The starting point for this substance was 1:1-dimethylcyclohexane-3:5-dione, which was prepared by a slight modification of the process of Vorländer (A.,

1897, i, 275); this substance is reduced by the gradual addition of sodium to a hot solution in absolute alcohol with the formation of 1:1-dimethylcyclohexane-3:5-diol, a sweet substance which separates from a mixture of benzene and acetone in lustrous, colourless needles. By heating with phosphorus tribromide in a sealed tube at 110—120°, this glycol is converted into 3:5-dibromo-1:1-dimethylcyclohexane, a colourless liquid, b. p. 120—122°/12 mm.,  $D_4^{20}$  1.5865,  $n_D^{20}$  1.5329, which can also be obtained, but less advantageously, by the action of hydrobromic acid on the glycol. Zinc dust acts readily on a warm aqueous-alcoholic solution of this dibromide with the formation of a second ring, the product being 3:3-dimethyl[0,1,3]-bicyclohexane,



This substance is a colourless liquid, b. p. 115° (corr.),  $D_4^{20}$  0.7962,  $n_D^{20}$  1.4331, which reacts vigorously with dry bromine, but only slightly with sulphuric acid diluted with half its bulk of water or also with cold dilute potassium permanganate solution. The formation of hydrogen bromide in the first reaction and the lack of change with the other reagents indicate the saturated nature of the hydrocarbon; in fact, treatment with potassium permanganate solution was resorted to as a means of removing small quantities of an olefinic cyclic hydrocarbon impurity. For the purpose of comparison, the isomeric 1:1-dimethyl-Δ<sup>3</sup>-cyclohexene (Crossley and Renouf, T., 1905, 87, 1491) was examined, and the following values obtained: b. p. 117—117.5° (corr.),  $D_4^{20}$  0.7994,  $n_D^{20}$  1.4430, the differences in the density and refractivity indicating the more saturated nature of the new substance.

When 3:3-dimethyl[0,1,3]-bicyclohexane is heated with hydriodic acid at 100—110°, an iodo-compound is obtained, which can be reduced in alcoholic solution by zinc dust, yielding a hydrocarbon which from its properties, b. p. 115—116°/760 mm.,  $D_4^{20}$  0.7703,  $n_D^{20}$  1.4223, and its indifference towards permanganate and bromine is probably 1:1:3-trimethylcyclopentane. That the fission of the trimethylene ring has occurred thus and not at the 2:6 linking is evidenced by the distinct nature of the otherwise expected *gem*-dimethylhexamethylene (Crossley, *loc. cit.*). Reduction by hydrogen under the catalytic influence of platinum-black at 125°, or by palladium-black at 55—60°, followed a quite different course, the product, b. p. 109.5—110.5° (corr.),  $D_4^{20}$  0.7403,  $n_D^{20}$  1.4088, being probably 1-methyl-2-isobutylcyclopropane. As might be expected (Zelinski, A., 1913, i, 254), reduction by hydrogen under the influence of nickel causes a more considerable change, and even with reduction at 95—100° the physical properties of the product indicate the admixture of the above cyclopropane derivative with an appreciable quantity of an octane.

D. F. T.

**Anhydrides of Aromatic Sulphonic Acids.** HANS MEYER and KARL SCHLEGL (*Monatsh.*, 1913, 34, 561—577).—The action of thionyl chloride on aromatic sulphonic acids presents another example of the very considerable effect of minute traces of foreign substances

on the course and products of a chemical change. The product may be, in this case, the sulphonic anhydride, the sulphonyl chloride, or a mixture of both; the variation is apparently due to traces of impurity in the thionyl chloride, but in the majority of cases investigated no trustworthy decision could be made as to the disturbing factor. The formation of chloride and anhydride appears to be concurrent.

The sulphonic acid anhydrides are colourless or pale yellow, crystalline solids, which are remarkably stable towards water and weak alkali. They react with alcohol, ammonia, and amines, producing the corresponding esters and amides; they can be sulphonated and nitrated. On account of their sparing solubility in indifferent organic solvents they can easily be separated from the very soluble acid chlorides. It is surprising that, although they are stable towards water in bulk, yet they become easily hydrated by moist solvents or by exposure to damp air. The thionyl chloride used for their preparation was purified by distillation over quinoline or dimethylaniline (compare Besthorn, A., 1909, i, 673), the remaining yellow coloration being removed by further successive distillations over linseed oil and pure bees-wax.

Benzenesulphonic acid when heated with excess of thionyl chloride passes into solution with loss of its water of crystallisation, and after further heating, the solution, when cooled, deposits a mixture of benzenesulphonyl chloride with the anhydride, m. p. 90—91° (Billetter, A., 1905, i, 584); the latter substance was usually the preponderating constituent, but occasionally, with apparently the same conditions, the case was the reverse. Silver benzenesulphonate reacts with thionyl chloride yielding the acid chloride as the sole product.

*p*-Bromobenzenesulphonic anhydride, obtained by heating the acid with thionyl chloride and pouring the reaction mixture into ice water, is a colourless, crystalline substance, m. p. 164—167° (decomp.).

2:5-Dibromobenzenesulphonic anhydride, obtained by a similar process to the last, is a crystalline powder (compare Rosenberg, A., 1886, 551).

*m*-Nitrobenzenesulphonic anhydride, obtained analogously, forms colourless crystals decomposing at 130—140°; the accompanying chloride had m. p. 58°.

*p*-Toluenesulphonic anhydride, crystals, m. p. 122—125°, is obtained together with the chloride by heating *p*-toluenesulphonic acid with pure thionyl chloride; if the thionyl chloride is not pure, the acid chloride is the sole product.

Mesitylenesulphonic anhydride is often obtained mixed with the corresponding chloride if mesitylenesulphonic acid is heated with commercial specimens of thionyl chloride. If the last substance has been purified the only product is the acid chloride, but the power to produce the anhydride is restored to the thionyl chloride by distilling it with sulphur chloride. Sodium mesitylenesulphonate behaves in the same curious manner with the various specimens of thionyl chloride.

*ψ*-Cumenesulphonic anhydride is obtained mixed with the corre-



sponding acid chloride under the reverse conditions to those observed in the last case. Purified thionyl chloride gives rise to a mixture of the acid anhydride and acid chloride, whilst the commercial substance yields the acid chloride only.

$\alpha$ -Naphthalenesulphonic anhydride could not be obtained as the corresponding acid and also the sodium salt of the acid were converted by thionyl chloride entirely into the acid chloride.

$\beta$ -Naphthalenesulphonic anhydride, a pale yellow, crystalline substance, is obtained together with the chloride, m. p. 73–74°, by the interaction of  $\beta$ -naphthalenesulphonic acid and excess of thionyl chloride.

$\alpha$ -Anthraquinonesulphonic acid, yellow crystals, m. p. 210–211°, and also the  $\beta$  isomeride are converted by thionyl chloride entirely into  $\alpha$ - and  $\beta$ -anthraquinonesulphonyl chlorides, crystalline solids, m. p. 203–204° and 185–187° respectively.

2-Chloro-5-nitrobenzenesulphonic anhydride forms colourless crystals, m. p. 120–125° (decomp.).

Ethanesulphonic acid with thionyl chloride yielded the acid chloride, whilst 3-pyridinesulphonic acid failed to react. D. F. T.

Tridiphenylmethyl. WILHELM SCHLENK (*Ber.*, 1913, 46, 1475–1481. Compare A., 1910, i, 236).—In reply to Schmidlin (this vol., i, 32) it is stated that the tridiphenylmethyl obtained earlier by the author (*loc. cit.*) is a homogeneous product, and that the supposed isomeride of Schmidlin is due to an impurity caused by the presence of 4:4'-dibromodiphenyl in the *p*-bromodiphenyl used. In the subsequent Grignard reaction by which the carbinol is produced, the former substance gives rise to 4:4'-diphenylene-bis-[bidiphenylcarbinol],  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Ph})_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\text{Ph})_2\cdot\text{OH}$ , which, mixed with tridiphenylcarbinol, constitutes Schmidlin's " $\beta$ -tridiphenylcarbinol."

4:4'-Diphenylene-bis-[bidiphenylcarbinol] can be obtained pure by the condensation of 4:4'-di-iododiphenyl with bisdiphenylketone and also of ethyl diphenyl-4:4'-dicarboxylate with iododiphenyl, in each case by the Grignard process. The substance is being more closely investigated. D. F. T.

$\alpha$ -Naphthylbisdiphenylmethyl. WILHELM SCHLENK and C. BORSCHARDT (*Ber.*, 1913, 46, 1482–1483).—Contrary to the opinion of Schmidlin and Bergmann (this vol., i, 46),  $\alpha$ -naphthylbisdiphenylcarbinol,  $\text{C}_{10}\text{H}_7\cdot\text{C}(\text{C}_6\text{H}_4\text{Ph})_2\cdot\text{OH}$ , can be readily obtained by the action of magnesium  $\alpha$ -naphthyl bromide on bisdiphenyl ketone; it forms prismatic crystals, m. p. 228°, which give a bluish-violet solution in sulphuric acid. When heated with a mixture of acetyl chloride and benzene, it is converted into chloro- $\alpha$ -naphthylbisdiphenylmethane,  $\text{C}_{10}\text{H}_7\cdot\text{C}(\text{C}_6\text{H}_4\text{Ph})_2\cdot\text{Cl}$ , m. p. 214–216°, which gives a deep blue solution in molten phenol. If the chloro-compound is heated in benzene solution with copper bronze under an atmosphere of carbon dioxide,  $\alpha$ -naphthylbisdiphenylmethyl is obtained, which separates from its brownish-red benzene solution as a greyish-green, crystalline powder. As a

solution of this substance which has been converted into the peroxide by shaking with air does not regain any of its original colour on keeping, it is probable that the substance is almost entirely unimolecular.

D. F. T.

**Preparation of Aromatic Nitroamino-compounds.** HEINRICH BART (D.R.P. 258059).—When 3-nitro-4-hydroxyazobenzene-4'-sulphonic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ , is reduced with iodine and sulphurous acid (or phosphorus) it furnishes sulphanilic acid and 3-nitro-*p*-aminophenol, glistening, red needles, m. p. 127°, whilst 3-nitro-aminophenol, together with 4-chloroaniline-3-sulphonic acid, is obtained in a similar manner from 3-nitro-4-hydroxy-4'-chloroazobenzene-3'-sulphonic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_3\cdot\text{Cl}\cdot\text{SO}_3\text{H}$ .

F. M. G. M.

**Preparation of 5-Chloro-6-amino-1-naphthol-3-sulphonic Acid.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.P. 258299).—When  $\beta$ -naphthylamine-5:7-disulphonic acid is treated with *p*-toluenesulphonyl chloride and the product subsequently chlorinated, it gives rise to 1-chloro-2-*p*-toluenesulphonylaminonaphthalene-5:7-disulphonic acid, a pale yellow, crystalline powder; when this is fused at 150—180° with potassium hydroxide, it furnishes 5-chloro-6-*p*-toluenesulphonylamino-1-naphthol-3-sulphonic acid, a red, crystalline powder, which when stirred into fuming sulphuric acid yields 5-chloro-6-amino-1-naphthol-3-sulphonic acid.

F. M. C. M.

**Preparation of Creosol (*p*-Hydroxytolyl 3-Methyl Ether).** SACCHARIN-FABRIK AKTIENGESellschaft VORM. FAHLBERG, LIST & CO. (D.R.P. 258105. Compare A., 1877, ii, 888; 1899, i, 346).—When homocatechol is treated with methyl sulphate, it furnishes a 70% yield of pure creosol together with 5—6% of homoveratrole.

F. M. G. M.

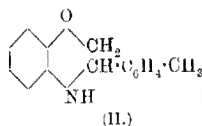
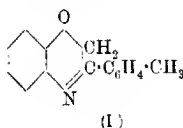
**Desmotropy of Phenols in the Anthracene Series.** ROLAND SCHOLL (*Ber.*, 1913, 46, 1442).—A claim for priority against Meyer and Schlösser (this vol., i, 295).

H. W.

Certain *p*-Toluoylemethyl, Phenyl-, Nitrophenyl-, Toly- and Naphthyl-ethers; 3-*p*-Tolyl-1:4-benzoxazine and 3-*p*-Tolyl-phenmorpholine and their Derivatives. FRANZ KUNCKEL [with KARL PULS] (*Ber. Deut. pharm. Ges.*, 1913, 23, 269—278).—A series of ethers has been prepared by the action of *p*-tolyl chloromethyl ketone,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , on the sodium or potassium salts of phenols.

*Phenyl-p-toluoylemethyl ether*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ , white needles, m. p. 73—75°, is prepared by boiling an alcoholic solution of *p*-tolyl chloromethyl ketone with an aqueous solution of potassium phenoxide. When dissolved in alcohol and treated with an excess of bromine water, it yields a monobromo-derivative,  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{Br}$ , needles, m. p. 105—107°. The similarly prepared *p*-nitrophenyl *p*-toluoylemethyl ether forms pale yellow leaflets, m. p. 165—166°, and is transformed by

phenylhydrazine in acetic acid solution into a somewhat unstable *phenylhydrazone*, yellow needles, m. p. 167—168°. *o*-Nitrophenyl *p*-toluoylmethyl ether is best obtained by heating an intimate mixture of dry potassium *o*-nitrophenoxide with *p*-tolyl chloromethyl ketone at 70°, and crystallises in yellowish-white needles, m. p. 123—124°. *p*-Chlorophenyl *p*-toluoylmethyl ether forms a white, crystalline powder, m. p. 123—124°. Phenyl *p*-toluoylmethyl sulphide, m. p. 64°, is obtained by heating a mixture of sodium phenyl sulphide and *p*-tolyl chloromethyl ketone with light petroleum at 80° during several hours. *m*-Tolyl *p*-toluoylmethyl ether, white leaflets, m. p. 72°, and *p*-tolyl *p*-toluoylmethyl ether, needles, m. p. 101—102°, are similarly prepared. *o*-Tolyl *p*-toluoylmethyl ether, needles, has m. p. 82°. *p*-Toluoylmethyl  $\beta$ -naphthyl ether, prepared by boiling an alcoholic solution of *p*-tolyl chloromethyl ketone



with a solution of  $\beta$ -naphthol in aqueous potassium hydroxide, forms colourless, rhombic crystals, m. p. 82—83°. The similarly obtained *p*-toluoylmethyl  $\alpha$ -naphthyl ether, m. p. 99—101°, yields with bromine in acetic acid solution a compound,  $C_{19}H_{15}O_2Br$ , silky needles, m. p. 148—150°.

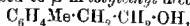
3-*p*-Tolyl 1:4-benzoxazine (formula I), m. p. 90—92°, is obtained by the reduction of a cold alcoholic solution of *o*-nitrophenyl *p*-toluoylmethyl ether by stannous chloride and fuming hydrochloric acid. Its hydrochloride was analysed. When the same ether is reduced at a higher temperature by tin and hydrochloric acid, 3-*p*-tolylphenmorpholine (formula II) is formed in white needles, m. p. 67—68°. It yields a nitroso-derivative, m. p. 101—102°. The hydrochloride, needles, m. p. 190—191°, and the platinumchloride, m. p. 180—182°, were analysed.

H. W.

**Syntheses in the Fatty Aromatic Series. IX.** JULIUS VON BRAUN, A. GRADOWSKI, and G. KIRSCHBAUM (*Ber.*, 1913, 46, 1266—1282. Compare A., 1912, i, 265; 1911, i, 830).—A systematic investigation of the effect of alterations in structure on the odour of the primary alcohols and aldehydes of the phenylethane and phenylpropane groups. It is found that the introduction of a methyl radicle into the benzene ring has very little effect, but that such substitution at the carbon atom adjacent to the carbinol or aldehyde group of phenylpropyl alcohol or phenylpropaldehyde causes a characteristic change in the odour; substitution of a methyl radicle into the corresponding position of the phenylethane derivatives or at the carbon atom adjacent to the benzene ring in the phenylpropane derivatives produces only a slight weakening of the odour of the parent substances.

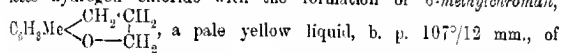
*m*-Xylyl bromide,  $C_6H_4MeCH_2Br$ , was converted through the cyanide into tolylethylamine, the benzoyl derivative of which when fused with phosphorus pentachloride and then distilled under reduced

pressure, undergoes decomposition into benzonitrile and *m*-tolylethyl chloride, a colourless liquid of pleasant odour, h. p. 112°/23 mm.; this on heating with sodium acetate and acetic acid for fifteen hours yields the corresponding *acetate*, a liquid of fruity odour, b. p. 130°/18 mm., which is easily hydrolysed to  $\beta$ -*m*-tolylethyl alcohol,



a liquid, h. p. 123—125°/18 mm.,  $D_4^{20}$  1.001, of a pleasant odour, resembling that of phenylethyl alcohol.

$\gamma$ -*m*-Tolylpropyl alcohol can be produced by a process similar to the last, but a more direct method is possible by starting with 6-methylquinoline or 8-methylquinoline; these can be reduced to the corresponding tetrahydroquinoline derivatives, which by the Schotten-Baumann reaction are converted into *benzoyl*-6-methyltetrahydroquinoline, m. p. 78°, and *benzoyl*-8-methyltetrahydroquinoline, needles, m. p. 100°, respectively. If these benzoyl compounds are caused to undergo scission by heating with phosphorus pentachloride (A., 1904, i, 918) they produce *benzo-o*- $\gamma$ -chloropropyl-*p*-toluidide, m. p. 151°, and *benzo-o*- $\gamma$ -chloropropyl-*o*-toluidide, m. p. 112°, which on cautious hydrolysis by hydrochloric acid in a sealed tube yield the hydrochlorides of *o*- $\gamma$ -chloropropyl-*p*-toluidine (hydrochloride, m. p. 183°) and *o*- $\gamma$ -chloropropyl-*o*-toluidine (hydrochloride, m. p. 172°; rod *platinichloride*, m. p. 197°). Diazotisation of chloropropyl-*p*-toluidine hydrochloride, followed by treatment with copper powder, gives rise to 6-chloro-3-methylphenylpropyl chloride,  $\text{CH}_3\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{C}_6\text{H}_3\text{MeCl}$ , b. p. 125°/9 mm., possessing an odour resembling that of orange rind. If chloropropyl-*p*-toluidine is diazotised in solution in sulphuric acid and the reaction product warmed, the resultant *chloropropyl-p-cresol* when heated with alkali loses hydrogen chloride with the formation of 6-methylchroman,



peppermint odour, which gives a red coloration with concentrated sulphuric acid. Reduction of a diazotised solution of the chloropropyl-toluidine hydrochloride by an alkaline solution of stannous chloride produces *m*-tolylpropyl chloride, b. p. 130°/14 mm., which can be converted through the *acetate*, b. p. 136°/10 mm., into  $\gamma$ -*m*-tolylpropyl alcohol,  $\text{C}_6\text{H}_4\text{Me}\cdot[\text{CH}_2]_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 140°/11 mm.,  $D_4^{20}$  0.9603, which closely resembles phenylpropyl alcohol in odour.

The most satisfactory starting point for  $\gamma$ -phenyl-*n*-butyl alcohol is acetophenone, which by condensation with zinc and ethyl bromoacetate followed by dehydration is converted into  $\beta$ -phenylcrotonic acid; this can be reduced to  $\beta$ -phenyl-*n*-butyric acid, the *ethyl ester*, b. p. 118°/9 mm., of which can be reduced by sodium and alcohol, giving a 60% yield of  $\gamma$ -phenyl-*n*-butyl alcohol,  $\text{CHMePh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 134°/16 mm.,  $D_4^{20}$  0.9834, which resembles phenylpropyl and phenylethyl alcohols in odour. When heated with hydrochloric acid, the alcohol yields the corresponding *chloride*, b. p. 114—116°/17 mm., which is remarkably resistant to the usual chemical agents; it gives no reaction with potassium acetate and acetic acid, and when treated in light petroleum with aluminium chloride is hardly affected, yielding only traces of a non-volatile hydrocarbon and of a hydrocarbon, b. p.

90—100°/10 mm., possibly methylhydrindene; even with sodium the reaction does not occur normally, as the product is *isobutylbenzene*, b. p. 174—175°,  $D_4^{20}$  0.8625.  $\gamma$ -Phenyl-*n*-butyl bromide, b. p. 108—110°/8 mm., can be obtained in a similar manner from the phenylbutyl alcohol, and reacts normally with ethyl sodiomalonate and ethyl sodioacetoacetate as well as with magnesium; the product from its slow reaction with sodium is a mixture of approximately equal quantities of *isobutylbenzene* and  $\beta\eta$ -diphenylacetone, a colourless liquid, b. p. 192—193°/10 mm.,  $D_4^{20}$  0.9539, resembling glycerol in appearance.  $\gamma$ -Phenylpropyl bromide, on the other hand, gives with sodium a 75% yield of  $\alpha\zeta$ -diphenylhexane.

$\gamma$ -Phenyl- $\beta$ -methylpropyl alcohol,  $\text{CH}_3\text{Ph}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , is a rather viscous oil, b. p. 128—129°/16 mm.,  $D_4^{20}$  0.9826, with an odour recalling linalool. It is obtained in 65% yield by the reduction of ethyl  $\beta$ -phenyl- $\alpha$ -methylpropionate by sodium and alcohol; the corresponding phenylmethylpropyl chloride, b. p. 112—114°/17 mm., is even less reactive than  $\gamma$ -phenyl-*n*-butyl chloride, for whilst the latter reacts with sodium iodide, the former fails to do so. The bromide, b. p. 110°/9 mm., however, behaves in a less abnormal manner, reacting with ethyl sodiomalonate and ethyl sodioacetoacetate; with sodium it reacts slowly, producing *isobutylbenzene* together with  $\beta$ -diphenylhexane, a viscous oil, b. p. 186—188°/8 mm.,  $D_4^{20}$  0.9457.

$\beta$ -Phenyl-*n*-propyl alcohol,  $\text{CHMePh}\cdot\text{CH}_2\cdot\text{OH}$ , can be obtained by the reduction of the corresponding aldehyde (hydratropaldehyde; Claisen, A., 1905, i, 286). An attempt to prepare it through a phenyl-ethyl bromide by the Grignard reaction miscarried, because the action of magnesium was merely synthetic, producing  $\beta\gamma$ -diphenylbutano, m. p. 121—122°. The chloride of the above alcohol was prepared by a series of changes, commencing with  $\beta$ -phenyl-*n*-butyric acid; this reacts with phosphorus pentachloride, producing the acid chloride, b. p. 114°/11 mm., which with ammonia in ethereal solution yields the amide, m. p. 98.5°; this amide can be converted by the usual process with hypobromite into  $\beta$ -phenyl-*n*-propylamine, b. p. 104°/21 mm.; yellow platinumchloride, m. p. 229° (decomp.); yellow picrate, m. p. 180°; benzoyl derivative, m. p. 85°. The last-named substance when fused with phosphorus pentachloride, and the mixture distilled under reduced pressure, gives a distillate which on hydrolysis with hydrochloric acid yields  $\beta$ -phenyl-*n*-propyl chloride, b. p. 98—100°/22 mm. The same chloride is obtained from benzo- $\alpha$ - $\beta$ -chloroisopropylamide (the scission product of 3-methyldihydroindole; von Braun and Kirschbaum, A., 1912, i, 499) by cautious hydrolysis with hydrochloric acid and reduction of the diazo-compound of the resultant  $\alpha$ - $\beta$ -chloroisopropylaniline by alkaline stannous chloride solution. The yield of chloride in these two methods of preparation is not very satisfactory, and the product is very unreactive, being completely unaffected by the acetates of the alkali metals or of silver.

$\beta$ -Phenyl-*n*-butaldehyde,  $\text{CHPhMe}\cdot\text{CH}_2\cdot\text{CHO}$ , was prepared by the "nitro" method, because in spite of its lack of reactivity,  $\gamma$ -phenyl-*n*-butyl chloride will undergo double decomposition with sodium iodide producing  $\gamma$ -phenyl-*n*-butyl iodide, a colourless liquid, b. p. 132°/14 mm.; this reacts in the usual manner with silver nitrate, and the reaction

mixture on distillation gives  $\gamma$ -phenyl-n-butyl nitrite, b. p. approx.  $120^{\circ}/12$  mm., and  $\alpha$ -nitro- $\gamma$ -phenyl-n-butane, b. p.  $138^{\circ}/12$  mm. The latter substance when treated in alcoholic solution with an equimolecular quantity of sodium hydroxide solution, and then with a solution of stannous chloride in hydrochloric acid, produces an oil which, after boiling with dilute sulphuric acid, yields  $\beta$ -phenyl-n-butaldehyde, b. p.  $110^{\circ}/9$  mm.; phenylhydrazone, oily; the odour of the substance is sharp, and recalls that of phenylacetaldehyde.

D. F. T.

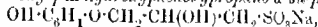
**Cholesterol. XVI. Methyl isohexyl Ketone, a Degradation Product of Cholesterol.** ADOLF WINDAUS and C. RESAU (*Ber.*, 1913, **46**, 1246—1248).—It has been observed by many workers that the oxidation of cholesterol by various methods is always accompanied by the formation of a substance of pleasant odour (compare Windaus, *A.*, 1909, i, 920). The odoriferous substance has now been isolated by collecting the distillate from a boiling solution of cholesterol acetate in acetic acid to which a solution of chromic acid was gradually added; acetic acid was removed from the distillate by sodium hydroxide solution, the liquid was again distilled, then dissolved in ether, and the acetone removed by shaking with water. Careful evaporation of the ether then gave a small residue of the pleasant smelling oil; semicarbazone, colourless, rectangular leaflets, m. p.  $153-154^{\circ}$ .

The composition,  $C_{17}H_{33}O$ , of the semicarbazone suggested that the parent substance is an octanone, and a comparison of the m. p.'s of the semicarbazones indicated that the odoriferous substance was methyl isohexyl ketone. For further confirmation, methyl isohexyl ketone (Darzens, *A.*, 1905, i, 172) was prepared (p-nitrophenylhydrazones, deep yellow crystals, m. p.  $83^{\circ}$ ), and the identity of the semicarbazones was satisfactorily established.

D. F. T.

**Preparation of Alkali Salts of m-Hydroxyphenoxypropane-sulphonic Acid.** ALBERT WOLFF (D.R.-P. 258473).—Sodium  $\gamma$ -chloro- $\beta$ -hydroxypropane- $\alpha$ -sulphonate,  $CH_2Cl \cdot CH(OH) \cdot CH_2 \cdot SO_3Na$ , hard, colourless crystals, is obtained when a boiling aqueous solution of sodium sulphite (252 parts) in 500 parts of water is treated with 128 parts of  $\alpha$ -dichlorohydrin.

Sodium  $\beta$ -hydroxy- $\gamma$ -m-hydroxyphenoxypropane- $\alpha$ -sulphonate,



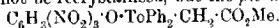
a colourless, crystalline powder, can be prepared in 50% yield by heating a concentrated solution of catechol (110 parts) in 56 parts of sodium hydroxide with 196 parts of the foregoing sodium chlorohydroxypropanesulphonate during two hours under reflux in the presence of an indifferent gas such as hydrogen.

F. M. G. M.

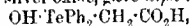
**Aromatic Telluretine Compounds. I.** KARL LEDERER (*Ber.*, 1913, **46**, 1358—1362).—Diphenyl telluride has been condensed with bromoacetic acid and its esters, and compounds analogous to dimethyltellurine bromide (Brown and Letts, *A.*, 1874, 980) and to phenylmethylselenetene bromide (Pope and Neville, *T.*, 1902, **81**, 1553) have been

obtained. The corresponding purely aromatic derivatives of sulphur and selenium could not be prepared.

Diphenyl telluride and methyl bromoacetate were left together for two or three days and then precipitated with ether. The methyl ester of diphenyltellurine bromide,  $\text{TePh}_2\text{Br}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , formed stout prisms from hot water, m. p. 105—106°. It was transformed by silver chloride into the chloride, m. p. 115—116°, with which zinc, gold, mercuric and platonic chlorides formed double salts. The chromate and dichromate could not be recrystallised, but the picrate,

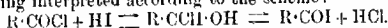


formed well-defined, yellow needles, m. p. 144—145°. The ethyl ester, m. p. 63—64°, from ethyl bromoacetate was resolved by boiling water into its components. Diphenyltellurine bromide,  $\text{TePh}_2\text{Br}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , itself was obtained from bromoacetic acid as a very hygroscopic mass, which, on shaking with silver oxide, gave diphenyltellurine,



in the form of needles, m. p. 117—118°. The esters were hydrolysed by, and gave the same compound with, silver oxide. J. C. W.

**Preparation and Reactions of Acid Haloids.** HERMANN STAUDINGER and E. ANTHES (*Ber.*, 1913, 46, 1417—1426).—Acid chlorides can be converted into the corresponding bromides or iodides by the action of an excess of hydrogen bromide or hydrogen iodide, the reaction being interpreted according to the scheme:



The analogous reaction with hydrocyanic acid does not appear to be applicable to the production of nitriles.

Acetyl chloride was converted into almost pure acetyl bromide by the action of dry hydrogen bromide, the yield being 80%. Similarly, cooled acetyl chloride and hydrogen iodide gave a 70% yield of acetyl iodide, b. p. 105—108°. Diphenylacetyl iodide, pale yellow crystals, m. p. 46°, obtained from hydrogen iodide and diphenylacetyl chloride, was far more sensitive to the action of moisture than the latter substance, and, when heated at 150°, was decomposed with an almost quantitative elimination of carbon monoxide.

Benzoyl chloride was incompletely transformed into the bromide at the ordinary temperature; completely, however, at 100°. Benzoyl iodide was readily obtained in 95% yield from benzoyl chloride and hydrogen iodide. It had b. p. 109—109.5°/10 mm., and was colourless when pure, rapidly becoming yellow when preserved. The rate of decomposition of the benzoyl haloids by water has been investigated by shaking dilute ethereal solutions with water at 0° and titration of the acid formed. The iodide was found to be more readily decomposed than the bromide, and the latter more readily than the chloride. It was also noticed that elimination of the halogen acid was incomplete (compare Straus and Hüsey, A., 1909, i, 490). This was attributed to decomposition of the benzoyl haloid by ether, but no ethyl iodide and only traces of ethyl benzoate could be detected. When ether was replaced by toluene or xylene, sharp differences in the behaviour of the haloids could not be detected, probably owing to the slight solubility of water in the hydrocarbons. When heated in a sealed tube for twenty

hours at 190°, benzoyl iodide yielded iodine, benzoic acid, and black, asphalt-like products, but no carbon monoxide. At 250°, carbon monoxide was not liberated. At 500°, however, under 15—25 mm. pressure, benzoyl iodide yielded iodobenzene and iodine, whilst at 700° still more pronounced decomposition occurred. Benzoyl bromide was stable at 500°, but yielded bromobenzene at 700°, whilst decomposition of benzoyl chloride did not occur even at 700°.

Benzoyl iodide reacted vigorously with benzaldehyde with formation of *iodobenzyl benzoate*,  $\text{Ph} \cdot (\text{CO})_2 \cdot \text{CHPh}$ . The product so obtained was contaminated with iodine and could not be purified owing to its extreme instability. It was obtained, however, in colourless crystals, m. p. about 60°, by mixing the reagents in light petroleum solution. Benzoyl bromide reacted slowly with benzaldehyde, bromobenzyl benzoate, m. p. 65°, being formed, whilst no compound was obtained from benzoyl chloride.

Benzoyl iodide was scarcely affected by treatment with dry hydrogen chloride for three hours, but, after fifteen hours, the presence of benzoyl chloride was ascertained.

Benzoyl iodide reacted slowly with mercury at the ordinary temperature. At 120—130° reaction was complete within two to three days. Benzil did not appear to be formed. The main products, particularly at the higher temperature, were brown resins and a substance, m. p. 40°, which has not yet been investigated. In benzene solution, reaction occurred more slowly. In ethereal solution a ready action was observed, the products of which were ethyl iodide and ethyl benzoate.

Hydrogen bromide did not react with carbonyl chloride even at 200°. Slight reaction was observed when hydrogen iodide was mixed with gaseous carbonyl chloride.

Hydrogen cyanide appeared to be without action on boiling acetyl chloride or on oxalyl chloride at 15—20°.

H. W.

**The Perkin Reaction.** HANS MEYER and ROBERT BEER (*Monatsh.*, 1913, 34, 649—658).—In spite of the earlier investigations, it is still not certain whether in the Perkin synthesis the reaction occurs between the aldehyde and the salt of the fatty acid, or whether the anhydride plays a primary part.

It is now demonstrated that the yield of unsaturated acid depends largely on the aldehyde used; with sodium acetate and acetic anhydride, *o*-iodobenzaldehyde, *o*-chlorobenzaldehyde, *o*-nitrobenzaldehyde, benzaldehyde and *p*-dimethylaminobenzaldehyde gave yields in decreasing order of magnitude; with potassium acetate and acetic anhydride the relative behaviour of the various aldehydes appears to be the same, but the yields are uniformly better.

A comparison of the yields obtained by using *o*-chlorobenzaldehyde with the acetates of various metals in the presence of acetic anhydride shows that the alkali metals give better results the higher the atomic weight; lead acetate gives results comparable with the acetates of the alkali metals; mercuric acetate is poorer, whilst the acetates of copper and of the alkaline earth metals produce very small yields of chlorocinnamic acid.



The presence of an acid anhydride is not indispensable: benzaldehyde heated for twenty-six hours with potassium acetate and acetic acid gives a 30% yield of cinnamic acid. The yields of unsaturated acid when *o*-chlorobenzaldehyde is heated with an acetate and acetic acid is usually somewhat smaller than when acetic anhydride is used, but rubidium and lead acetates gave actually slightly better yields with the acid than with the anhydride. Michael's view (A., 1901, i, 358) that the Perkin reaction occurs between aldehyde and acid anhydride is, therefore, untenable.

The rôle of the acetic acid in the immediately preceding experiments appears to be merely that of solvent, and it is found that a 40% yield of unsaturated acid can be obtained by heating together *o*-chlorobenzaldehyde and potassium acetate, without the addition of a third substance, to 240° for thirty-six hours.

D. F. T.

**The Halogen-Substituted Cinnamic Acids and their Behaviour in Ultra-violet Light.** RICHARD STOERMER and PAUL HEYMANN (*Ber.*, 1913, 46, 1249—1266. Compare A., 1912, i, 974).—In reply to Liebermann (this vol., i, 265), the authors submit that the former's proof of the structure of *allo*-cinnamic acid is not above suspicion, and that the nature of his experiments renders his decision merely a probability. The action of sulphuric acid on *allo*-cinnamic acid yields only ordinary cinnamic acid, and even if fuming sulphuric acid is used, the main product under suitable conditions is ordinary cinnamic acid accompanied by a relatively very small quantity of truxone (compare Liebermann, A., 1898, i, 662). It is also already recognised that there are exceptions to Liebermann's method of deciding the constitution of these isomerides by physical properties.

The main portion of the paper consists of the results of an extension of the investigation of the behaviour of ethylenic stereoisomerides in ultra-violet light (Stoerner, A., 1911, i, 295; 1910, i, 114).

*α*-Chlorocinnamic acid (Sudborough and James, T., 1906, 89, 107), m. p. 137° (*aniline* salt, needles, m. p. 137°), exposed in acetic acid solution to the ultra-violet rays from a mercury lamp for twenty-one days is converted to the extent of 21% into *allo-α*-chlorocinnamic acid, m. p. 111° (*aniline* salt, needles, m. p. 96°). In a similar manner in methyl alcoholic solution, *α*-chlorocinnamamide, m. p. 121°, is converted to the extent of 10% into the amide (m. p. 134°) of the *allo*-acid in ten days.

*α*-Bromocinnamic acid, m. p. 131° (*aniline* salt, needles, m. p. 132°), when exposed in acetic acid to ultra-violet rays for twenty-one days is converted to the extent of 10% into *allo-α*-bromocinnamic acid, m. p. 120° (*aniline* salt, scales, m. p. 102°). When a methyl alcoholic solution of the *allo*-acid was exposed to ultra-violet rays, 71% was converted into the more stable isomeride. Similarly, *α*-bromocinnamamide, leaflets, m. p. 117°, in methyl-alcoholic solution is converted into the *allo*-isomeride (needles, m. p. 129°; 24% in 240 hours); the latter substance under similar treatment is re-converted to the extent of 50% into the original amide.

*β*-Bromocinnamic acid, needles or leaflets, m. p. 135°, is readily pro-

duced by submitting the *allo*-isomeride (Erlenmeyer, A., 1896, i, 46) in chloroform solution containing a little bromine to the action of sunlight; the product is an equilibrium mixture. The action of ultra-violet rays on an acetic acid solution for thirty-five days converted 40% of the acid into the *allo*-isomeride, m. p. 159–160°. Ultra-violet illumination converted 75% of the *allo*-acid in ethyl acetate solution into the ordinary acid.

Of the two  $\beta$ -chlorocinnamic acids, m. p. 142° and 132° respectively, the latter from its similarity to the analogous bromo-compound must be the *allo*-isomeride (compare Michael and Pendleton, A., 1889, 1063). The acetic acid solution of the former (*trans*-) compound is converted to the extent of 40% in twenty-one days into the *allo*-isomeride; the *aniline* salt, like that of *allo*- $\beta$ -bromocinnamic acid, is unstable. In contact with bromine in sunlight the *allo*-acid is slowly re-converted into the other form.

The authors discontinue the use of the term *allo* in connexion with the  $\alpha\beta$ -dihalogen-substituted cinnamic acids, because the compounds which from their power of indone formation must be the *cis*-isomerides are more stable than the *trans*-isomerides.

*cis*- $\alpha\beta$ -Dichlorocinnamic acid, m. p. 121° (*aniline* salt, needles, m. p. 129°), when treated with cold sulphuric acid yields dichloroindone.

When a solution in acetic acid is submitted to ultra-violet rays for twenty-one days, 45% of the acid undergoes conversion into the hitherto unknown *trans*- $\alpha\beta$ -dichlorocinnamic acid, rhombic tablets, m. p. 101°; *barium* salt, woolly needles; *aniline* salt, needles, m. p. 121°. The *trans*-acid is also obtained by the elimination of hydrogen chloride from the dichloride of  $\alpha$ -chlorocinnamic acid by the action of potassium hydroxide solution; it is separated from the *cis*-isomeride simultaneously formed by the sparing solubility of the *potassium* salt of the *trans*-acid in alcohol. The action of sunlight on a chloroform solution of the *trans*-acid containing a little bromine causes a re-conversion into the *cis*-isomeride.

The action of bromine on phenylpropionic acid solution in carbon disulphide in the absence of sunlight produces a mixture of *cis*- $\alpha\beta$ -dibromocinnamic acid, yellow prisms, m. p. 100°; with the isomeric *trans*-acid, scales, m. p. 136°, in approximately the proportion 2:1; the two acids give *aniline* salts, needles, m. p. 126° and 128° respectively. In chloroform solution containing bromine, sunlight causes a partial change of the *trans*- into the *cis*-isomeride, but as the latter always predominates in the equilibrium mixture, it may be regarded as the more stable (compare Roser and Haselhoff, A., 1888, 1304). In ultra-violet light, the *cis*-acid, dissolved in acetic acid, is converted into the *trans*-acid to the extent of 40% in fourteen days. This *cis*-acid is converted by cold sulphuric acid into dibromoindone, but a much better method for the production of this substance is the action of aluminium chloride on the corresponding acid chloride in carbon disulphide solution at water-bath temperature; under these conditions a quantitative yield of dibromoindone, m. p. 123°, is obtained.

$\alpha\beta$ -Diiodocinnamic acid, m. p. 171° (Liebermann and Sachse, A., 1892, 470), decomposes when exposed in solution to ultra-violet rays; consequently no isomerisation could be detected; from the fact that the

known acid gives no indone formation with sulphuric acid, it is presumably of the *trans*-configuration.

Curves are given illustrating the course of the isomerisation of the acids, and the properties of the various acids are tabulated.

D. E. T.

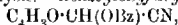
**The Constitution of Abietic Acid.** PAUL LEVY (*Zeitsch. anorg. Chem.*, 1913, 81, 145—155).—The evidence for the constitution of abietic acid is reviewed and a few new experiments described. Oxidation with nitric acid yields dinitropropane and *trans*-cyclohexane-1:2-dicarboxylic acid. Abietic acid is related to roteuic and pinene, contains a cyclohexane ring and an isopropyl group, and has its carboxyl group attached to a tertiary carbon atom. None of the formulæ hitherto proposed conforms to all these conditions, with the exception of that due to Easterfield and Bagley (*T.*, 1904, 85, 1241).

C. H. D.

**Benzoylated Cyanohydrins and Amides from Aldehydes, and the Corresponding Hydroxyacids.** JULES ALOY and CHARLES RABAUT (*Bull. Soc. chim.*, 1913, [iv], 13, 457—460. Compare A., 1912, i, 462).—The preparation of benzoylated cyanohydrins by the action of benzoyl chloride on a mixture of an aldehyde with aqueous potassium cyanide has been extended to the fatty and heterocyclic series.

*Benzoylglycollonitrile* [*Benzoyloxyacetoneitrile*],  $\text{OBz}\cdot\text{CH}_2\cdot\text{CN}$ , from formaldehyde, forms well-defined, stable crystals, m. p.  $26-27^\circ$ , b. p.  $275^\circ$  or  $165^\circ/25$  mm., which dissolve in concentrated hydrochloric acid or slightly warmed 60% sulphuric acid with the formation of *benzoyloxyacetamide*,  $\text{CO}\cdot\text{NH}_2\cdot\text{CH}_2\cdot\text{OBz}$ , in hard, lustrous crystals, m. p.  $117-118^\circ$ . Hydrolysis by hot dilute sodium hydroxide provides a convenient method for the preparation of glycollic acid, but when an insufficient quantity of very dilute alkali is employed and the reaction is arrested as soon as ammonia ceases to be liberated, benzoyloxyacetic acid, m. p.  $79^\circ$ , results. The silver salt was analysed. Alcoholic ammonia converts the nitrile into benzamide and the amide into benzamide and glycollamide. Sodium ethoxide causes no replacement by sodium in the  $-\text{CH}_2$  group, but yields sodium cyanide and benzoate and ethyl benzoate, and in the case of benzoylmandelonitrile gives rise to benzoin.

Similarly, *a*-benzoyloxybutyronitrile is obtained from propaldehyde as an impure oil, which gives a *benzoyloxybutyramide*,  $\text{OBz}\cdot\text{CH(Et)}\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $92^\circ$ , and finally sodium *a*-hydroxybutyrate on hydrolysis, whilst *a*-benzoyloxyisovaleronitrile,  $\text{CHMe}_2\cdot\text{CH}(\text{OBz})\cdot\text{CN}$ , from isobutaldehyde, has m. p.  $21-22^\circ$ , and gives the *amide*, m. p.  $98^\circ$ , and then *a*-hydroxyisovaleric acid on hydrolysis. *Benzoyloxyfurylacetonitrile*,



from furfuraldehyde, has m. p.  $47-48^\circ$ , but hydrolysis led to discoloured, indefinite substances.

The reaction is being extended to the ketones, in which case prolonged agitation is necessary (compare Francis and Davis, *T.*, 1909, 95, 1403; 1910, 97, 949).

J. C. W.

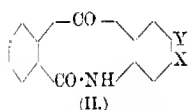
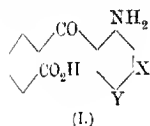
Racemisation of Tropic Acid and its Esters, together with a Theory of Racemisation, Substitution, and the Walden Inversion. JOHANNES GADAMER (*J. pr. Chem.*, 1913, [ii], 87, 312—332).—This paper contains a full and detailed account of the author's theory, a short description of which has already appeared (*A.*, 1912, i, 934; compare Frankland, Presidential Address, T., 1913, 103, 722—725).

[With MAX KUNTZE.]—*Ethyl l-tropate*, prepared from ethyl iodide and silver *l*-tropate, has  $[\alpha]_D^{20} - 47.5^\circ$  in alcoholic solution; the *d*-ester has  $[\alpha]_D^{20} + 46.6^\circ$ .

Experiments are also described to show that the conversion of hyoscyamine into atropine is due to ionisation at the asymmetric atom.

F. B.

Preparation of an Inner Anhydride (Lactam) of 2 Amino-benzoyl-*o*-benzoic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.P. 258343).—When the 2-amino-benzoyl-*o*-benzoic acids of the general formula I (where X and Y may be hydrogen, methyl, a halogen or carboxylic group) are heated either alone



with condensing agents or with solvents of high boiling point, they readily lose water and furnish inner anhydrides (lactams) of general formula II, and which are readily hydrolysed by alkali-hydroxides to regenerate the parent substance.

When 2-amino-benzoyl-*o*-benzoic acid, rhombic crystals, m. p.  $195^\circ$  (with formation of the lactam), is heated at  $200^\circ$  with nitrobenzene it furnishes the corresponding lactam, m. p.  $245^\circ$ ; the base accompanied by another isomeride is obtained by the nitration and subsequent reduction of benzoyl-*o*-benzoic acid and separation effected by means of the calcium salts.

2:5-Diaminobenzoyl-*o*-benzoic acid, yellow needles, m. p.  $265^\circ$ , is obtained by heating 2-amino-5-acetylaminobenzoyl-*o*-benzoic acid (prepared by the nitration and subsequent reduction of 3-acetylaminobenzoyl-*o*-benzoic acid) with 30% sulphuric acid and subsequent decomposition of the lactam thus formed.

2-Amino-5-acetyl-amino-4-carboxybenzoyl-*o*-benzoic acid, yellow needles, m. p.  $315^\circ$ , is obtained by the oxidation (with potassium permanganate) of 2-nitro-5-acetyl-amino-4-toluoyl-*o*-benzoic acid and reduction of the so-obtained 2-nitro-5-acetyl-amino-4-carboxybenzoyl-*o*-benzoic acid, m. p.  $247^\circ$ ; when heated with 30% sulphuric acid the foregoing amino-acetyl-amino-base furnishes the sulphate of 2:5-diamino-4-carboxybenzoyl-*o*-benzoic acid, m. p.  $340^\circ$  (about), together with its lactam.

F. M. G. M.

Reduction of the Anhydrides and Imides of Phthalic and Naphthalic Acids. ARNOLD REISSERT (*Ber.*, 1913, 46, 1184—1491).—The reduction of phthalic anhydride by zinc dust and acetic acid is known to give a complex mixture, from which diphthalyl, hydro-

diphthalyl-lactonic acid and phthalide can be isolated (Wislicenus, A., 1885, 57), whilst reduction by distillation with zinc dust yields a mixture of zinc phthalate and diphthalyl.

It is now discovered that when phthalic anhydride is gradually introduced into an agitated suspension of zinc dust in a solution of calcium chloride in 40% alcohol at 20—22° about half is converted into phthalic acid and half into diphtalyl-lactonic acid, for which

the author prefers the formula  $\text{CO} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ .

No satisfactory method for the preparation of phthalide from phthalic anhydride could be discovered, but it was found that phthalimide can be reduced by stirring with a suspension of zinc dust in cold 2*N*-sodium hydroxide solution with the production of *hydroxy-*

*phthalimidine* (compare Gräbe, A., 1885, 979),  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NH}$ ,

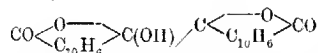
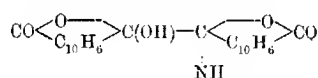
needles, m. p. 171—172°, which on boiling with acetic acid is converted into a *substance*, needles, m. p. 240—241°, of which the structure is probably  $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CH} \cdot \text{C}(\text{OH}) \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NH}$ . It

after the reduction of phthalimide to hydroxyphthalimidine the reaction mixture containing excess of zinc is heated, a further reduction occurs and ammonia is liberated with the production of phthalide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{O}$ , in almost theoretical yield.

If naphthalic anhydride is shaken with zinc dust and 2*N*-sodium hydroxide solution, a blue solution is obtained, which on addition of more alkali and further shaking becomes red; on neutralisation a reddish-yellow, crystalline *substance*,  $\text{C}_{24}\text{H}_{12}\text{O}_5$ , m. p. 213—215°, is precipitated, whilst the naphthalic acid produced simultaneously remains in solution. The coloured reduction product, which the author designates *deocynaphthalic anhydride*, possibly of the formula

$\text{CO} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{CO}$ , gives an unstable blue colour with

sodium carbonate solution and a stable red one with sodium



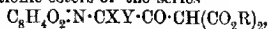
solves in alkali solutions with a bright blue or violet colour.

The reduction of naphthalimide by a similar process to that which was successful with phthalimide yielded only a pasty product.

D. F. T.

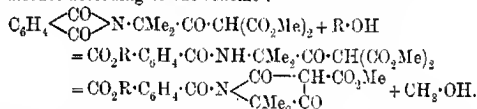
Action of Acylamino-acid Chlorides on the Sodium Compounds of the Esters of Malonic and Cyanoacetic Acids. SIEGMUND GAMMEL (*Ber.*, 1913, 46, 1319—1358).—A number of

phthaliminoacylmalonic esters of the series



where X and Y = H or alkyl, have been prepared from acylamino-chlorides. It is found that the stability of the esters is enhanced when X and Y represent 1 or 2 alkyl groups, the non-substituted compounds having the character of strong acids and losing one  $-CO_2R$  group on boiling with water (A., 1909, i, 491; 1911, i, 212). The presence of these groups is also a criterion for the pyrrolone condensation (A., 1911, i, 227), which also occurs when the malonic ester group is replaced by  $-CH_2 \cdot CN$ ,  $-CH_2 \cdot CO \cdot NH_2$ , or by methyl, and when a benzoyl nucleus is substituted for the phthalyl group.

The same substituted phthaliminoacylmalonic esters are peculiar in their behaviour towards sodium alkyl oxides, for the yellow sodium compound of the ester changes into the colourless neutral salt of a strong acid. Phenoxyacylmalonic esters underwent no such isomerism, whereas benzoylaminoisobutyryl chloride condensed with methyl sodiomalonate to form a strongly acid compound with one methyl alcohol group less than the expected malonic ester. Benzoylmethylaminoisobutyryl chloride, on the other hand, gave the malonic ester, from which it appears that an unsubstituted imino-group is necessary for the formation of the acidic compounds. These are shown to be derivatives of tetramic acid (Anschütz, A., 1912, i, 836), and their formation from methyl phthaliminoisobutyrylmalonate, for example, presupposes the preliminary opening of the phthalyl ring and the addition of alcohol according to the scheme:

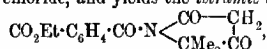


This is supported by synthesis and by the fact that the methyl ethyl ester obtained from the methyl malonate and sodium ethoxide on the one hand, and from the ethyl malonate and sodium methoxide on the other, were isomeric. All these tetramic acid derivatives lose the ester group which is attached to the tetramic acid ring on hydrolysis with very dilute acids, and are decomposed by hydriodic acid into phthalic acid, alkyl iodide, carbon dioxide, and aminomethylbutanone.

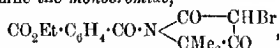
[With JAMES COLMAN and KARL A. BÖTTCHER.]—For the preparation of ethyl phthaliminoisobutyrylmalonate (A., 1911, i, 213), it is recommended to use enough ethyl sodiomalonate to form the sodium compound of the new ester. This forms light yellow needles, and gives a yellow, alkaline solution which is decomposed by carbon dioxide. The ethyl alcoholic solution or the solution of the free ester mixed with sodium ethoxide gradually becomes pale in the cold, quickly on warming, and on evaporation deposits the white, isomeric sodium salt,  $C_{13}H_{20}O_2 \cdot NNa$ , which gives a neutral solution and is only decomposed by mineral acids, when *ethyl carbethoxybenzoyldimethyltetramcarboxylate* [2 : 4-diketo-1-benzoyl-5 : 5-dimethylpyrrolidine-o-3-dicarboxylate],

$CO_2Et \cdot C_6H_4 \cdot CO \cdot N \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} CH \cdot CO_2Et$ , is formed as a crystalline

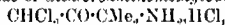
powder, m. p. 81°. It has a strongly acid reaction, gives an orange-red colour with ferric chloride, and yields the *tetramic acid*,



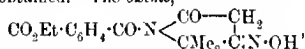
on hydrolysis with warm dilute hydrochloric acid as a white powder, m. p. 198—199°, which disengages carbon dioxide from barium carbonate, gives a red coloration with ferric chloride, and an ammonium salt, in slender, white needles. The acid gives with one molecule of bromine the *monobromide*,



m. p. 159—160°, from glacial acetic acid, which forms a hydrate with  $1\text{H}_2\text{O}$  in rhombic needles, m. p. 121—122°, from dilute acetic acid, and yields phthalic acid and *bromoaminomethylbutanone hydrobromide*,  $\text{CH}_3\text{Br}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{NH}_2\cdot\text{HBr}$ , in leaflets, m. p. 156°, on boiling with hydrobromic acid. This ketone reduces Fehling's solution and forms a *picrate*, which gives a turbid liquid at 135° becoming clear at 147°. Excess of bromine gives the *tribromide*,  $\text{C}_{16}\text{H}_{15}\text{O}_5\text{NBr}_3$ , m. p. 155°, which is neutral and can no longer become enolic. Chlorine yields the neutral *dichloride* in flat needles, m. p. 126—126.5°, from which the *hydrochloride of dichloroaminomethylbutanone*,



m. p. 203°, was obtained. The *oxime*,

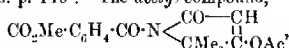


forms microscopic crystals, m. p. 193°.

When the initial ethyl malonate is treated with sodium methoxide or when the sodium compound is left with methyl alcohol, the white, microcrystalline, neutral sodium salt,  $\text{C}_{18}\text{H}_{18}\text{O}_5\text{NNa}$ , is obtained, from which hydrochloric acid precipitates *ethyl carbonmethoxybenzoyldimethyltetramcarboxylate* [methyl ethyl 2:4-diketo-1-benzoyl-5:5-dimethylpyrrolidine-0.3-dicarboxylate],  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N} \begin{array}{l} \text{CO}-\text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CMe}_2\cdot\text{CO} \end{array}$ , which

forms colourless needles, m. p. 133—134°, gives a copper and a silver salt, and, on hydrolysis, the *tetramic acid*,  $\text{C}_{15}\text{H}_{15}\text{O}_5\text{N}$ , in needles, m. p. 210—211°. The acid distils unchanged in a vacuum, yields an ammonium salt, an *oxime*,  $\text{C}_{15}\text{H}_{16}\text{O}_5\text{N}_2$ , in sparkling prisms, m. p. 210°, and a *hydrazone*,  $\text{C}_{15}\text{H}_{17}\text{O}_5\text{N}_3$ , in short prisms, m. p. 222—223°. The

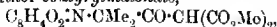
*methyl ether*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N} \begin{array}{l} \text{CO}-\text{CH} \\ \text{CMe}_2\cdot\text{C}\cdot\text{OMe} \end{array}$ , is obtained by the action of methyl alcohol and hydrogen chloride as a crystalline powder, m. p. 103—104°, which gives no colour with ferric chloride, is insoluble in alkalis, and yields a *bromo-derivative*,  $\text{C}_{16}\text{H}_{16}\text{O}_5\text{NBr}$ , in matted needles, m. p. 140°. The *acetyl compound*,



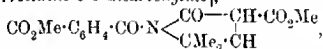
forms crystalline granules, m. p. 119—120°. The *monobromo-derivative* forms flat, rectangular prisms, m. p. 221°, which yield an ammonium salt and the above bromoaminomethylbutanone hydro-

bromide. The *dibromo-derivative* forms glistening needles, m. p. 193°, and the *dichloride*, m. p. 172—173°, yields the above dichloro-aminomethylbutanone salt on hydrolysis.

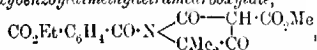
*Methyl phthaliminoinobutrylmalonate*,



forms colourless, rhombohedral crystals, m. p. 91°, which give a dark cherry-red colour with ferric chloride. The *sodium* compound is yellow, reacts alkaline, and changes in methyl alcohol into the colourless, neutral *isomeride*, from which hydrochloric acid liberates *methyl carboethoxybenzoyldimethyltetramcarboxylate* [2:4-diketo-1-benzoyl-5:5-dimethylpyrrolidine-o-3-dicarboxylate],

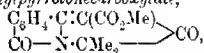


in short, thick columns, m. p. 155°, which may be distilled in a vacuum. It forms a *silver* salt, and gives the above tetramic acid, m. p. 210—211°, on hydrolysis. In order to synthesise the compound, *aminoisobutyric acid* was condensed with the chloride of methyl hydrogen phthalate (Meyer, A., 1901, i, 750) to form *carboethoxybenzoylaminoisobutyric acid*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , in rhombic tablets, m. p. 168°. This was converted into the *chloride* by means of thionyl chloride, and then condensed with methyl sodiomalonate and the product identified with the expected ester, m. p. 155°. When the methyl ester, m. p. 91°, is allowed to react with sodium ethoxide, the neutral *sodium* salt of *methyl carboethoxybenzoyldimethyltetramcarboxylate*,

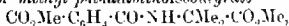


is formed as a granular powder, m. p. 99°, which gives a *copper* salt. In contrast to its isomeride, m. p. 133—134°, its tetramic acid derivative is the ethyl compound, m. p. 199°, and not the methyl, m. p. 210—211°.

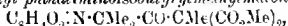
The methyl ester, m. p. 91°, but not so the isomeride, m. p. 155°, condenses in presence of methyl sodiomalonate in boiling benzene to *methyl benzoylenedimethylpyrrolonecarboxylate*,



in yellow needles, m. p. 165° (compare the ethyl ester, A., 1911, i, 213). Similarly, phthaliminomethylbutanone (*ibid.*) gave benzoylenedimethylpyrrolone (A., 1911, i, 228). *Methyl phthaliminoinobutrylate*,  $\text{C}_6\text{H}_4\text{O}_2\text{:N}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Me}$ , prepared from the chloride in colourless, rhombic plates, m. p. 78°, combined with methyl alcohol when left with that liquid or when warmed with sodium methoxide solution, and gave the *methyl ester* of *methyl phthalaminoinobutrylate*



in delicate needles, m. p. 116—117°, thus behaving differently, as was expected, from the phthaliminooacetates and propionates, which give *isoquinoline* derivatives (A., 1900, i, 358). The methyl ester, m. p. 91°, may also be methylated by the action of methyl iodide on the sodium compound. *Methyl phthalaminoinobutrylmethylmalonate*,



forms prisms, m. p. 121°, and on hydrolysis with hydrochloric acid yields *aminomethylpentanone hydrochloride*,  $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{NH}_2\cdot\text{HCl}$ ,



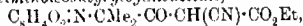
in rectangular tablets, m. p. 164°. The *hydriodide*,  $C_8H_{10}ON, HI$ , crystallises in needles, m. p. 141–142°, and gives a *picrate*, m. p. 145°. The *benzoyl* derivative forms silky needles, m. p. 118°, and the *phthalyl* compound crystallises in rhombic tablets, m. p. 70°, whilst the free base,  $C_8H_9 \cdot CO \cdot CMe_2 \cdot NH_2$ , is a colourless, mobile liquid, which, unlike aminomethylbutanone, but like aminoisobutyrophenone (A., 1911, i, 212), distils without condensation, b. p. 157.5°/762 mm.

$\alpha$ -Phthalylalanyl chloride (A., 1908, i, 182) has also been condensed with ethyl sodiomalonate, forming a light yellow *sodium* compound, from which carbon dioxide separated *ethyl  $\alpha$ -phthalylalanyl malonate*,  $C_8H_9O_5 \cdot N \cdot CHMe \cdot CO \cdot CH(CO_2Et)_2$ , in rhombic plates, m. p. 73–74°. Contrary to the above phthaliminoisobutyrylmalonates, it did not form a tetramic or a pyrrolone derivative. When hydrolysed by means of fuming hydriodic acid, methyl  $\alpha$ -aminoethyl ketone *hydriodide*,  $C_4H_9NO, HI$ , m. p. 89°, is formed (Künne, A., 1895, i, 685), but hydrobromic acid at 70° led to  *$\alpha$ -phthaliminoethyl methyl ketone*,  $C_8H_9O_5 \cdot N \cdot CHMe \cdot COMe$ , which formed flat leaflets, m. p. 85–86°.

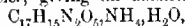
Phenoxyacetyl chloride was also condensed with methyl sodiomalonate, when the new *sodium* salt was obtained in silky, white needles, from which carbon dioxide separated *methyl phenoxyacetyl malonate*,  $OPh \cdot CH_2 \cdot CO \cdot CH(CO_2Me)_2$ , as an oil.

Similarly, *phenoxyisobutyryl chloride*,  $OPh \cdot CMe_2 \cdot COCl$ , a colourless oil, b. p. 112–113°/12.5 mm., yielded *ethyl  $\alpha$ -phenoxyisobutyrylmalonate*,  $OPh \cdot CMe_2 \cdot CO \cdot CH(CO_2Et)_2$ , in prisms, m. p. 69°. The chloride was obtained from ethyl phenoxyisobutyrate, b. p. 127°/12 mm. (compare Bischoff, A., 1906, i, 346), by the action of phosphorus pentachloride on the free acid, and yielded the *amide*,  $OPh \cdot CMe_2 \cdot CO \cdot NH_2$ , in silky needles, m. p. 116°.

*Ethyl  $\alpha$ -phthaliminoisobutyrylcyanacetate*,

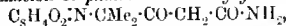


was obtained by adding phthaliminoisobutyryl chloride to ethyl sodiocyanacetate suspended in benzene, and decomposing the new light yellow salt with hydrochloric acid. It forms flat leaflets, m. p. 111°, and has acidic properties, giving an *ammonium* salt,

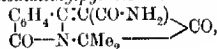


and a *copper* salt. On hydrolysis with dilute hydrochloric acid it yields  *$\alpha$ -phthaliminoisobutyrylacetonitrile*,  $C_8H_9O_5 \cdot N \cdot CMe_2 \cdot CO \cdot CH_2 \cdot CN$ , in long needles, m. p. 154°. When left or warmed with dilute alkalis the substance loses water and forms *o-benzoylenecyanodimethylpyrrolone*,

$C_8H_7 \cdot C : C(CN) \cdot CO$  in yellow prisms, m. p. 273°, which are converted by hydrobromic acid into benzoylenedimethylpyrrolone (*loc. cit.*). The nitrile also dissolves in cold concentrated sulphuric acid with the formation of *phthaliminoisobutyrylacetamide*,

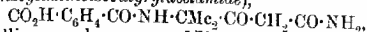


in long, flat needles, m. p. 136°. This compound condenses very readily to *o-benzoylenedimethylpyrrolonecarbonamide*,



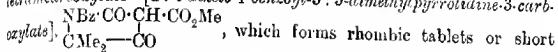
which forms long, yellow prisms, m. p. 217°. When warmed with

concentrated sulphuric acid, however, the nitrile takes up  $2\text{H}_2\text{O}$  and forms the *phthaloylic acid* derivative of *aminoisobutyrylacetylamide* (*o-carboxybenzoylaminoisobutyrylacetylamide*),



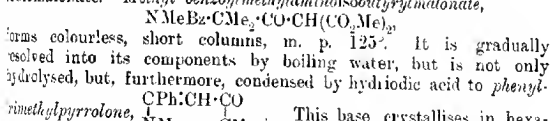
as a crystalline powder, m. p.  $171^\circ$ , which merely dissolves and undergoes no condensation in alkalis.

Benzoylaminoisobutyric acid (dimethylhippuric acid) was prepared by benzoylating aminoisobutyric acid in acetone in presence of pyridine and then converted into the chloride (Mohr, A., 1910, i, 117). The latter was condensed with methyl sodiummalonate, when the expected ester was not obtained, but rather *methyl benzoyldimethyl-tetramicarboxylate* [2:4-diketo-1 benzoyl-5:5-dimethylpyrrolidine-3-carboxylate],



prisms, m. p.  $154\text{--}155^\circ$ . The substance had an acid reaction, dissolved in ammonia, and gave a copper salt and an orange-red coloration with ferric chloride. Hydrolysis with hydrochloric or hydriodic acid gave the salts of aminomethylbutanone. The analogous *ethyl ester*,  $\text{C}_{10}\text{H}_{17}\text{O}_5\text{N}$ , forms short prisms, m. p.  $111^\circ$ . Condensation of the above chloride with ethyl cyanoacetate, however, followed a normal course, and led to *ethyl benzoylaminoisobutyryl-cyanoacetate*,  $\text{NBz}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , which formed colourless rhombohedra, m. p.  $165^\circ$ . The compound forms salts with ammonia and silver, and gives a cherry-red coloration with ferric chloride. Hydrolysis with hydrochloric acid leads to *benzoylaminoisobutyryl-acetonitrile*,  $\text{NBz}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ , which forms long needles.

For the condensation of malonic esters with benzoylmethylaminoisobutyryl chloride, methylaminoisobutyric acid, prepared by a modification of Zelinsky and Stadnikoff's general method (A., 1906, i, 425), was benzoylated as above, the *benzoylmethylaminoisobutyryl acid*,  $\text{NMeBz}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , short prisms, m. p.  $183^\circ$ , was treated with thionyl chloride, and the crude product left with methyl sodiummalonate. *Methyl benzoylmethylaminoisobutyrylmalonate*,



This base crystallises in hexagonal tablets, m. p.  $100^\circ$ , b. p.  $346\text{--}347^\circ/768\text{ mm.}$ , and forms a soluble chloride, a sparingly soluble nitrate, iodide and picrate, m. p.  $147^\circ$ , and a platinichloride.

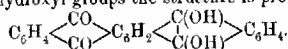
J. C. W.

Condensation of Pyromellitic Anhydride with Benzene and with Toluene. II. ERNST PHILIPPI (*Monatsh.*, 1913, 34, 705--717. Compare A., 1911, i, 793; Mills and Mills, T., 1912, 101, 2194).—It has not been found possible to produce substances analogous to anthranol in the dinaphthantraceno group by intramolecular elimination of water from reduced derivatives of dibenzoylbenzenedicarboxylic acids.

In the condensation of dibenzoylbenzenedicarboxylic acids to di-phthaloylbenzene by concentrated sulphuric acid, 2-benzoylanthraquinone-

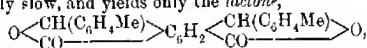
3-carboxylic acid, m. p. 283—285°, is obtained as a by-product, but by allowing the reaction to proceed at a lower temperature for a shorter period this substance becomes the main product; the *sodium* and *potassium* salts are sparingly soluble. Reduction of the acid with ammoniacal zinc dust and copper sulphate solution gives a poor yield of 2-benzylanthracene-3-carboxylic acid, m. p. 235—237°, which can be further reduced by hydriodic acid and phosphorus to 1:5-dibenzylbenzene-2:4-dicarboxylic acid, which decomposes without melting. No dianthranol nor any other condensation product could be obtained by heating this substance with sulphuric acid.

Reduction of dipthaloylbenzene by distillation with zinc dust in an atmosphere of hydrogen under reduced pressure and also by alkaline byposulphite yielded a sparingly soluble, reddish-brown, crystalline solid; this was unaltered by a temperature of 360°, and from the presence of two hydroxyl groups the structure is probably



The product of reduction of dipthaloylbenzene with hydriodic acid and phosphorus was exceedingly difficult to purify; it is an almost colourless substance, m. p. 210—215° (decomp.), the composition of which indicates a formula  $\text{C}_{22}\text{H}_{20}$ .

The condensation of pyromellitic anhydride with toluene by means of aluminium chloride proceeds in exactly the same way as with benzene; the reaction product is a mixture of two acids of the structure  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{CO}_2\text{H})_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , namely, 1:5-di-*p*-toluylbenzene-2:4-dicarboxylic acid and 1:4-di-*p*-toluyl-2:5-benzenedicarboxylic acid, which can be separated by fractional crystallisation from nitrobenzene; the former acid has m. p. 245—248°, whilst the latter and less soluble acid decomposes without melting. Reduction of the more soluble isomeride by zinc dust and copper in alkaline solution is exceedingly slow, and yields only the lactone,



a yellow solid which does not melt below 240°. The same lactone is also obtained when the reducing agent is a mixture of phosphorus and hydriodic acid, but in this case it is accompanied by 1:5-di-*p*-tolylbenzene-2:4-dicarboxylic acid, a yellow solid, m. p. near 238°.

D. F. T.

Hydrogenation of Santonin in Presence of Palladium Black  
(GIUDO BARGELLINI *Atti R. Accad. Lincei*, 1913, [v], 22, i, 413—447).

—The action of hydrogen on an alcoholic solution of santonin in the presence of palladium black yields a dihydrosantonin and a tetrahydrosantonin. The alcoholic solution of santonin containing palladium black is treated with hydrogen at 40—50 cm. pressure until the volume corresponding with the dihydro-compound has been absorbed (for 5 grams this takes fifteen to twenty minutes). The dihydrosantonin,  $\text{C}_{15}\text{H}_{20}\text{O}_5$ , so obtained, has m. p. 148—150°,  $[\alpha]_D^{25} + 23^\circ$  (in 2:105% alcoholic solution), and gives with alcoholic potassium hydroxide a yellow solution having a green fluorescence. It yields a semicarbazone,  $\text{C}_{15}\text{H}_{23}\text{O}_5\text{N}_3$ , which forms microscopic needles, m. p. 238—239°.

When the hydrogenation is continued until a further equal amount of hydrogen has been absorbed, a *tetrahydrosantonin*,  $C_{12}H_{22}O_3$ , is obtained; it forms colourless laminae, m. p. 154—155°,  $[\alpha]_D + 61.5^\circ$  (in 2.234% alcoholic solution). This substance does not become yellow when exposed to light, and is stable towards permanganate; it yields no coloration with potassium hydroxide.

R. V. S.

**Combination of Phenolcarboxylic Acids. III. FERDINAND MAUTHNER** (*J. pr. Chem.*, 1913, [iii], 87, 409—415).—A continuation of previous work (*A.*, 1911, i, 725; 1912, i, 267).

*Methyl p-3:5-dimethoxybenzoyloxybenzoate*, prepared by shaking an ethereal solution of 3:5-dimethoxybenzoyl chloride with methyl *p*-hydroxybenzoate dissolved in aqueous sodium hydroxide, crystallises in colourless needles, m. p. 91—92°. *Methyl m-3:5-dimethoxybenzoyloxybenzoate*, from methyl *m*-hydroxybenzoate, has m. p. 66—67°.

*Methyl m-3:5-dimethoxybenzoyloxy-p-methoxybenzoate*, from 3:5-dimethoxybenzoyl chloride and methyl vanillate, has m. p. 89—90°.

*Methyl 2-(3':5')-dimethoxybenzoyloxy-3-naphthoate*, from methyl 2-hydroxy-3-naphthoate, has m. p. 119—120°.

3:4:5-Trimethoxybenzoyl chloride reacts with methyl *m*-hydroxybenzoate, yielding *methyl m-3:4:5-trimethoxybenzoyloxybenzoate*, m. p. 143—144°, and with methyl 2-hydroxy-3-naphthoate to form *methyl 2-(3':4':5')-trimethoxybenzoyloxy-3-naphthoate*, m. p. 149—150°.

*Methyl m-4-methoxybenzoyloxybenzoate*, prepared from anisoyl chloride and methyl *m*-hydroxybenzoate, has m. p. 79—80°.

All the compounds described above crystallise in colourless needles.

The 3:4:5:2':6'-pentamethyl ether of dimethyl gallate (*A.*, 1911, i, 725) has m. p. 173—174°.

F. B.

**Tetra alkylation of cyclohexanone and  $\beta$ -Methylcyclohexanone and Trialkylation of Menthone.** ALBIN HALLER (*Compt. rend.*, 1913, 156, 1199—1206. Compare *A.*, 1908, i, 987; 1909, i, 108, 654; 1910, i, 219, 300; 1912, i, 269).—By the use of sodamide as condensing agent, all the hydrogen atoms attached to the two carbon atoms adjacent to the ketone group in the substituted or non-substituted cyclohexanones can be substituted by alkyl groups, chiefly methyl and allyl, condensation of the cyclohexanone on itself taking place to a certain extent at the same time. This latter condensation is increased if the methyl iodide is replaced by its higher homologues for substitution. The tetra-, penta-, and hexa-alkylcyclohexanones so obtained give neither oximes nor semicarbazones. The substitution is performed by dissolving the ketone (1 mol.) in anhydrous ether, or preferably toluene in some cases, adding the sodamide (1 mol.) in fine powder, and when all action has ceased adding the alkyl iodide in theoretical quantity. On the crude product obtained by treatment with water and then drying, this treatment is repeated two or three times. By this means the following compounds have been prepared:

1:1:3:3-Tetramethylcyclohexan-2-one,  $C_{12}H_{22}O \begin{smallmatrix} (CH_3 \cdot CMe_3) \\ CH_2 \cdot CMe_2 \end{smallmatrix} CO$ , b. p. 185—186°,  $D_{17}^{20} 0.8936$ ,  $n_D^{20} 1.447$ , which on reduction with sodium

VOL. CIV. i.

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and alcohol gives the corresponding *alcohol*, b. p. 195—197°/767 mm.,  $D^{17}_D$  0.9001,  $n^{20}_D$  1.455, giving a *phenylurethane*, m. p. 97—98°.

Attempts to prepare the ethyl derivatives by similar methods gave a mixture of small quantities of mono- and di-ethyl derivatives and a large amount of other condensation products.

1:1:3:3-Tetra-allylcyclohexan-2-one, b. p. 170—171°/18 mm.,  $D^{17}_D$  0.9490,  $n^{20}_D$  1.4920, giving on reduction the secondary *alcohol*, b. p. 171—173°/15 mm.,  $D^{15}_D$  0.9523,  $n^{20}_D$  1.4975, which gave no phenylurethane.

1:2:2:4:4-Pentamethylcyclohexan-3-one (compare A., 1905, i, 214, 602) was prepared in an active and inactive form. The active ketone had b. p. 201—202°/765 mm., 93—94°/23 mm.,  $D^{20}_D$  0.8979,  $n^{20}_D$  1.4515,  $[\alpha]_D + 24.0^\circ$ , and gave the corresponding *alcohol*, b. p. 210—212°/767 mm., giving a *phenylurethane*, m. p. 105—106°. The inactive ketone had b. p. 202—203°/765 mm.,  $D^{15}_D$  0.8997,  $n^{20}_D$  1.4553, and gave the *alcohol*, m. p. 45°, b. p. 213—214°/767 mm., yielding a *phenylurethane*, m. p. 127°.

1-Methyl-2:2:4:4-tetra-allylcyclohexan-3-one, b. p. 165—169°/12 mm.,  $D^{15}_D$  0.954,  $[\alpha]_D + 36.17^\circ$ , on reduction yields the corresponding *alcohol*, b. p. 187—189°/25 mm.,  $D^{17}_D$  0.9613,  $n^{20}_D$  1.5054,  $[\alpha]_D - 9.52^\circ$ , which yields no phenylurethane.

The alkylation of the menthones in order to pass beyond the mono-alkyl stage had to be carried out in toluene as a solvent. The products so obtained were:

Dimethylmenthone, b. p. 108—109°/14 mm., which on reduction gave the *alcohol*, b. p. 245—247°,  $[\alpha]_D + 3.23^\circ$ , yielding a *phenylurethane*, m. p. 90—91°. Attempts to prepare trimethylmenthone were not successful.

Diallylmenthone has b. p. 146—147°/13 mm.,  $[\alpha]_D + 25.50^\circ$ .

Triallylmenthone has b. p. 166—167°/14 mm.,  $[\alpha]_D + 6.40^\circ$ . W. G.

Arylsulphonylacetonates, Arylsulphonylacetonphenones, and Cyanobenzylarylsulphonates. JULIUS TRÖGER and O. BECK (*J. pr. Chem.*, 1913, [ii], 87, 289—311. Compare this vol., i, 169).—A number of arylsulphonylacetonphenones,  $SO_2R \cdot CH_2 \cdot COPh$ , and arylsulphonylacetonates,  $SO_2R \cdot CH_2 \cdot COMe$ , have been prepared by the interaction of the sodium salts of arylsulphonic acids with  $\alpha$ -chloroacetophenone and chloroacetone respectively. They resemble the arylsulphonylacetonitriles described previously (A., 1905, i, 336, 870), in that they dissolve in aqueous alkali hydroxides, and are reprecipitated unchanged by mineral acids. The mobility of the methylene hydrogen atoms in the arylsulphonyl-ketones is, however, not so great as in the case of the arylsulphonylacetonitriles, since condensation products with amyl nitrite and aromatic aldehydes could not be obtained.

Attempts to prepare arylsulphonylacetonphenones by the action of magnesium phenyl bromide on the corresponding arylsulphonylacetonitriles proved unsuccessful, the latter compounds being recovered from the reaction unchanged. Acetonitrile and phenylacetonitrile readily react with magnesium phenyl bromide, yielding acetophenone and decybenzoin respectively. In the case of chloroacetophenone, which should give rise to  $\alpha$ -chloroacetophenone, no definite compound

could be isolated from the reaction product. A similar retarding influence of the arylsulphonyl group has been observed with the arylsulphonylacetophenones, which do not react with organo-magnesium compounds, whereas acetophenone readily reacts with magnesium phenyl bromide and magnesium methyl iodide, yielding diphenyl-methylcarbinol and phenyldimethylcarbinol respectively.

*o*-Methoxybenzenesulphonylacetone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COMe}$ , prepared by heating sodium *o*-methoxybenzenesulphinate with chloroacetone in alcoholic solution, forms white, prismatic needles, m. p.  $65^\circ$ , and yields an *oxime*, m. p.  $160\cdot5^\circ$ .

*p*-Ethoxybenzenesulphonylacetophenone, obtained from sodium *p*-ethoxybenzenesulphinate in a similar manner, crystallises in white needles, m. p.  $67\cdot5^\circ$ ; the *oxime* forms leaflets, m. p.  $127^\circ$ . The following compounds were prepared by heating *o*-chloroacetophenone with the sodium salts of arylsulphonic acids in alcoholic solution: *benzenesulphonylacetophenone*,  $\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COPh}$ , which crystallises in white needles, m. p.  $96^\circ$ , and forms an *oxime*, m. p.  $134^\circ$ , a *semicarbazone*, m. p.  $194\cdot5^\circ$ , and a *phenylhydrazone*, yellow needles, m. p.  $170^\circ$ ; *p*-chlorobenzenesulphonylacetophenone, white needles, m. p.  $132\text{--}133^\circ$  (*oxime*, m. p.  $131\text{--}132^\circ$ ); *a*-naphthalenesulphonylacetophenone forms white needles, m. p.  $89^\circ$ , and yields an *oxime*, m. p.  $173^\circ$ , and a *phenylhydrazone*, yellow, prismatic columns, m. p.  $191\text{--}192^\circ$ ; *p*-toluenesulphonylacetophenone, m. p.  $110^\circ$  (*semicarbazone*, m. p.  $208\cdot5^\circ$ ); *o*-methoxybenzenesulphonylacetophenone forms stout, prismatic crystals, m. p.  $79^\circ$ , and yields a *phenylhydrazone*, crystallising in yellow prisms, which become yellowish-red at  $165^\circ$ , m. p.  $167\cdot5^\circ$ ; *p*-ethoxybenzenesulphonylacetophenone, white, prismatic needles, m. p.  $130^\circ$  (*oxime*, m. p.  $150^\circ$ ).

*o*-Benzenesulphonyl-*p*-toluonitrile,  $\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ , obtained by the interaction of *o*-chloro-*p*-toluonitrile and sodium benzenesulphinate in alcoholic solution, crystallises in white needles, m. p.  $204\cdot5^\circ$ . The following sulphones were prepared in a similar manner: *o*-*p*-chlorobenzenesulphonyl-*p*-toluonitrile, m. p.  $148\cdot5^\circ$ ; *o*-*p*-toluenesulphonyl-*p*-toluonitrile, prismatic needles, m. p.  $211^\circ$ ; *o*-*a*-naphthalenesulphonyl-*p*-toluonitrile, m. p.  $162\cdot5^\circ$ ; *o*-methoxybenzenesulphonyl-*p*-toluonitrile, m. p.  $121^\circ$ ; *o*-*p*-ethoxybenzenesulphonyl-*p*-toluonitrile, m. p.  $164^\circ$ . The above-mentioned sulphones differ from the arylsulphonyl-ketones and nitriles in being insoluble in aqueous alkali hydroxides. F. B.

The Friedel-Crafts Reaction. VI. (GUSTAV HELLER (*Ber.*, 1913, 46, 1437—1504. Compare A., 1912, i, 357, 358; etc.).—It has already been shown (A., 1912, i, 358; 1908, i, 991) that, whereas, *o*- and *p*-chlorotoluenes react normally with phthalic anhydride in the presence of aluminium chloride, the three bromotoluenes behave anomalously, yielding the same *o*-bromotoluoylbenzoic acid. The behaviour of the chloro- and bromo-toluenes with benzoyl chloride and aluminium chloride has therefore now been investigated.

[With LEOPOLD BUD.]—Benzoyl chloride was introduced into a well cooled mixture of *o*-chlorotoluene and aluminium chloride, and the mixture subsequently warmed; the product was a *phenyl chlorotolyl ketone*,  $\text{C}_6\text{H}_5\text{MeCl}\cdot\text{COPh}$ , colourless leaflets, m. p.  $82\text{--}83^\circ$ , which

was oxidised by chromium trioxide in acetic acid solution to a *chlorobenzophenonecarboxylic acid*, leaflets, m. p. indistinct at 187°. In a similar manner *p*-chlorotoluene gave rise to an isomeric *phenyl chlorotolyl ketone*, m. p. 35–36°, by the oxidation of which no characteristic acid could be obtained.

*p*-Bromotoluene, as also the *m*-isomeride, again exhibit anomalous behaviour, producing under similar conditions to the above only uncrystallisable oils, which from their inconstant b. p. must be mixtures caused probably by a wandering of the substituent groups during the reaction. On the other hand, *o*-bromotoluene gave an oily product which partly crystallised to a yellow solid, m. p. 173°, a *phenyl hydroxytolyl ketone*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{COPh}$ ; this is the first case of the replacement of bromine by hydroxyl in a Friedel-Crafts reaction, and as the primary reaction occurred in the absence of water, the hydroxy-compound must have been produced from an intermediate substance during the subsequent treatment.

The interaction of phenol, aluminium chloride, and benzoyl chloride yielded a mixture of 4-hydroxydiphenyl-ketone and phenyl benzoate. *o*-Cresol gave the same phenyl hydroxytolyl ketone (*acetyl* derivative, needles, m. p. 68–69°) as was obtained in the above reaction with *o*-bromotoluene. *m*-Cresol produced a yellow oil, from which could be separated two isomeric *phenyl hydroxytolyl ketones*, yellow crystals, m. p. 63°, and colourless needles, m. p. 129° (compare Bartolotti, A., 1901, i, 36), respectively, and *m*-tolyl benzoate. The product obtained with *p*-cresol was exclusively *p*-tolyl benzoate.

It has already been shown that phthalic anhydride condenses with  $\beta$ -chloronaphthalene in the presence of aluminium chloride with the formation of an acid, which by dehydration gives a ketone (Heller and Grünthal, A., 1912, i, 357). Oxidation of the ketone by a mixture of potassium permanganate and nitric acid yielded anthraquinone-2:3-dicarboxylic acid; the ketone must therefore be of the structure  

$$2\text{-chloro-6:7-phthaloylnaphthalene, } \text{C}_{10}\text{H}_4\left\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\right\rangle\text{C}_{10}\text{H}_5\text{Cl, and the acid}$$
 must be an *o*- $\beta$ -chloronaphthylbenzoic acid,  $\text{C}_{10}\text{H}_5\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ .  
 D. F. T.

**The Condensation of 2:5-Dimethoxybenzoyl Chloride with Phenolic Ethers.** FERDINAND MAUTNER (*J. pr. Chem.*, 1913, [5] 87, 403–409).—An account of the preparation of a number of methoxybenzophenones from 2:5-dimethoxybenzoyl chloride and phenolic ethers by means of the Friedel-Crafts reaction.

2:5-Dimethoxybenzoic acid is best prepared by methylating *o*-resorcylic acid with methyl sulphate and aqueous sodium hydroxide at the ordinary temperature; the chloride has b. p. 157–158°/16 mm. m. p. 35–36° (compare Kostancek and Lampe, A., 1908, i, 412); the *amide* and *anilide* crystallise in lustrous, silky needles, m. p. 148–149 and 124–125° respectively.

3:5:4'-Trimethoxybenzophenone, prepared from the chloride and anisole in carbon disulphide solution in the presence of aluminium chloride, forms colourless needles, m. p. 97–98°.

3:5:3':4'-*Tetramethoxybenzophenone*, obtained from veratrole in a similar manner, crystallises in colourless needles, m. p. 114—115°.

3:5:2':4'-*Tetramethoxybenzophenone*, from resorcinol dimethyl ether, forms needles, m. p. 73—74°.

2'-*Hydroxy*-3:5:3':4'-*tetramethoxybenzophenone*, prepared from pyrogallol trimethyl ether, forms light yellow crystals, m. p. 123—124°.

3:5:2':4':6'-*Pentamethoxybenzophenone*, from phloroglucinol trimethyl ether, crystallises in small needles, m. p. 132—133°. F. B.

**Benzilbenzoin.** ALFRED BENRATH (*J. pr. Chem.*, 1913, [ii], 87, 416—422).—Klinger's benzilbenzoin (A., 1886, 888) is produced by the photochemical reduction of benzil in solutions of aldehydes and aromatic hydrocarbons (compare Benrath, A., 1906, i, 535). When heated alone or in solution it decomposes into benzoin and benzil. Owing to this decomposition it has no definite m. p.; it begins to soften at 86°, and is completely fused at a temperature dependent on the rate of heating, the highest recorded temperature being 143°. A mixture of benzil and benzoin in equimolecular proportions shows the same m. p. interval as benzilbenzoin, and hence the latter compound must have the formula  $\text{COPh}\cdot\text{COPh}, \text{COPh}\cdot\text{CHPh}\cdot\text{OH}$ .

The fusion curve of mixtures of benzoin and benzil is recorded; it shows a eutectic point at 86°. F. B.

**Preparation of Derivatives of *p*-Benzoquinone.** FARBERKE VON MEISTER, LUCIUS & BRÜNING (D.R.-P. 257834).—When *p*-benzoquinone, its homologues, or halogen derivatives are boiled with naphthylaminesulphonic acids in the presence of sodium acetate they yield compounds which, after further condensation with zinc chloride (or concentrated sulphuric acid), dye wood or silk in reddish-violet to blue shades.

The tinctorial properties of the *disulphonaphthylaminodichlorobenzoquinones* thus obtained from chloroanil with  $\beta$ -naphthylamine-5- and -8-sulphonic acids are tabulated in the original. F. M. G. M.

**Preparation of a Derivative of Anthraquinone.** FARBERKE VON MEISTER, LUCIUS & BRÜNING (D.R.-P. 258439).—When 1-aminoanthraquinone (10 parts) dissolved in 500 parts of cooled 60% sulphuric acid is slowly treated with sodium chlorate (2 parts) dissolved in 40 parts of the same solvent, a blue coloration is rapidly developed, followed by the separation of a deep blue precipitate which can be purified by boiling with alcohol and crystallisation from nitrobenzene.

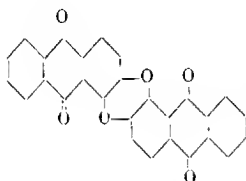
This compound is not apparently obtained when other oxidising agents are employed; it gives a colourless "vat" with alkaline hyposulphite, and on further reduction with stannous chloride furnishes leucoquinizarin. F. M. G. M.

**Behaviour of Dibenzoyl-1:5-dibenzylaminoanthraquinone with Alkaline Sodium Hyposulphite.** CHRISTIAN SEER (*Monatsh.*, 1913, 34, 579).—A correction; dibenzoyl-1:5-dibenzylaminoanthraquinone is not reduced by alkaline hyposulphite as previously stated (A., 1912, i, 571). D. F. T.



Preparation of Di- and Tri-anthrimides of the  $\beta$ -Anthraquinone Series. FARBERKE VORM. MEISTER, LUCIUS & BUCHING (D.R.-P. 257811).—It is found that dianthrimide can be prepared by heating together  $\beta$ -aminoanthraquinone (22.3 parts),  $\beta$ -chloroanthraquinone (24.2 parts), and potassium carbonate (7 parts) at  $300^\circ$ , whilst trianthrimide, a brown powder, is obtained in a similar manner from 2:6-diaminoanthraquinone (1 mol.) and  $\beta$ -chloroanthraquinone (2 mols.) or from  $\beta$ -aminoanthraquinone and 2:7-dichloroanthraquinone.

F. M. G. M.



[Preparation of an Anthraquinone Derivative.] R. WEDEKING & Co. (D.R.-P. 257832).—The compound (annexed formula) is obtained by the condensation of 1-chloro-2-hydroxyanthraquinone; it crystallises from nitrobenzene, does not melt at  $300^\circ$ , and furnishes cotton dyes.

F. M. G. M.

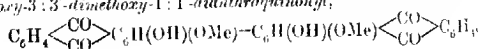
Attempts to Prepare a 3:4:3':4'-Tetrahydroxy-1:1'-dianthraquinonyl. CHRISTIAN SEER and KARL EHRENREICH (*Monatsh.*, 1913, 34, 631—648).—An unsuccessful endeavour to prepare a tetrahydroxyanthraquinonyl with the hydroxyl groups disposed in the same positions as in alizarin (compare Scholl and Seer, A., 1911, i, 453).

4-Aminoalizarin proved useless as a starting point, as it was found impossible to convert this through the diazo-compound into 4-iodoalizarin.

Alizarin dimethyl ether (1:2-dimethoxyanthraquinone) can be nitrated at  $0^\circ$  by potassium nitrate and sulphuric acid, or by nitric acid (D 151), with the formation of 4-nitro-1:2-dimethoxyanthraquinone, deep yellow, prismatic needles, which give a red solution in sulphuric acid. This substance when suspended in aqueous ammonium sulphide at  $100^\circ$  is reduced to 4-amino-1:2-dimethoxyanthraquinone, deep red needles, m. p.  $182-185^\circ$ , the hydrochloride of which, after diazotisation in acetic acid and treatment with aqueous potassium iodide solution, is converted into 4-iodo-1:2-dimethoxyanthraquinone, yellowish-brown, prismatic needles, m. p.  $172-174^\circ$ . The position of the iodo-group in this, and therefore of the nitro-group in the earlier substance, is proved by its red solution in sulphuric acid changing to a deep green (due to the formation of 3:4:3':4'-tetramethoxy- $\mu$ -benzo-

dianthrone,  $\text{CO} \begin{array}{c} \diagup \text{C}_6\text{H}(\text{OMe})_2 \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{C} = \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}(\text{OMe})_2 \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{CO}$ ; compare

Scholl and Mansfeld, A., 1910, i, 494) when treated with copper powder. Attempts to achieve the desired aim of the research by heating the iodo-compound with aluminium chloride at  $150-160^\circ$  eliminated only two methoxy-groups with the formation of 4:4'-dihydroxy-3:3'-dimethoxy-1:1'-dianthraquinonyl,

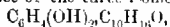


microscopic, orange-red prisms, which sublimes above  $320^{\circ}$ ; it dissolves in alkali to a bluish-violet colour, which changes to red on addition of sodium hyposulphite.

Another attempt to achieve the object of the investigation was made by Scholl and Seer's method with phthalic anhydride (*loc. cit.*). For this purpose veratrole was nitrated to 4-nitro-1:2-dimethoxybenzene, and this was reduced by tin and hydrochloric acid. Reduction at water-bath temperature produced, however, a halogen-substituted amino-compound, 2(1)-chloro-4:5-dimethoxyaniline, colourless needles, m. p.  $72-73^{\circ}$ ; hydrochloride, needles, which slowly decompose above  $150^{\circ}$ ; this was converted by diazotisation and potassium iodide into 2(1)-chloro-1-iodo-4:5-dimethoxybenzene, colourless needles, m. p.  $69-70^{\circ}$ , which, on heating with copper powder at  $270-280^{\circ}$  in an atmosphere of carbon dioxide, was converted into 6(1):6(1)-dichloro-3:4:3':4'-tetramethoxydiphenyl, colourless needles, m. p.  $160-161^{\circ}$ , soluble in sulphuric acid to a green solution. The successful reduction of nitrodimethoxybenzene to 4:5-dimethoxyaniline could be effected by the gradual addition of tin to the suspension of the solid in hydrochloric acid, and the product could then be converted into 1-iodo-4:5-dimethoxybenzene, but it was found that this substance can be more conveniently obtained by the action of iodine and mercuric oxide on an alcoholic solution of veratrole at the ordinary temperature. When heated with copper powder at  $260^{\circ}$ , the iodo compound is converted into 3:4:3':4'-tetramethoxydiphenyl, colourless, silky needles, m. p.  $130-132^{\circ}$ , the solution of which in sulphuric acid passes slowly from golden-yellow to emerald-green. It was not found possible to prepare from the last substance a tetrahydroxydianthraquinonyl of the desired structure; heating with phthalic anhydride and aluminium chloride yielded a complex, deep blue mixture in which the desired substance was probably present.

D. F. T.

Camphor and Phenols. I. Compounds of Camphor with Quinol, Resorcinol, and Catechol. N. N. KOREMOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 348-362).—Thermal and micrographic examination of mixtures of camphor with the three dihydroxybenzenes demonstrates the existence of the three isomeric compounds,



melting without decomposition at  $29.0^{\circ}$  (ortho) and  $11.5^{\circ}$  (meta) respectively. The compound with quinol also melts without decomposing, but it does not correspond with a maximum on the melting-point curve.

The dihydroxybenzenes form with camphor solid solutions containing for resorcinol, 20.0%, for catechol, 15%, and for quinol 37.5%, by weight of camphor.

The eutectic mixtures formed by camphor with the dihydroxybenzenes are viscous liquids prone to supercooling, and crystallise slowly only at  $-15^{\circ}$  to  $-20^{\circ}$  in spherulites having a fine granular structure. In each case the eutectic mixture contains 66.6 mols.% of camphor and has a characteristic yellow colour.

I. H. P.

The Constitution of "Terpineol-35-glycuronic Acid." JUNO HAMALAINEN (*Biochem. Zeitsch.*, 1913, 50, 220-222).—The conjugation

of the terpineol with glycuronic acid takes place with the scission of water. The author has administered the alcohol to rabbits, and succeeded in insulating the acid from the urine in the form of the anhydrous sodium salt,  $C_{10}H_{16}O_7Na$ . The urine was first precipitated with normal and then with basic lead acetate. The precipitate from the latter contained the lead salt of the glycuronate; from this the barium salt was obtained, and was crystallised from a water-alcohol-ether mixture. By treatment of this with the theoretical amount of sodium sulphate, a crystalline hydrated sodium salt was prepared.

S. B. S.

**Essential Oil of *Crithmum maritimum* (Linn.) from Sardinia.** LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 231—237, 312—317).—The oil of this plant from Sardinia differs from that from a French source described by Delépine, A., 1909, i, 642; 1910, i, 401).—Details are given of the properties of various fractions of the oil and of the yield from different parts of the plant. The chemical investigation of the oil shows that the only constituents common to both *aro* dillapiole and *p*-cymene. The *d*-pinene, dipentene, and thymol methyl ether of the French oil are not present in the other, which contains, however,  $\beta$ -phellandrene and a new terpene, to which the name *crithmene* is applied. There is also a white substance crystallising in leaflets, m. p. 63°, which has the properties of a paraffin.

Crithmene yields an  $\alpha$ -nitrosochloride, which crystallises in laminae, m. p. 101—102°, and a  $\beta$ -nitrosochloride,  $C_{10}H_{16}ONCl$ , which forms quadratic plates, m. p. 103—104°; both are optically inactive. The *tetrabromide* is oily. The *nitrolpiperides* prepared from the nitrosochlorides have m. p. 138°. The compound with *benzylamine* has m. p. 103—104°. When the nitrosochloride is decomposed with alcoholic potassium hydroxide and distilled in steam, a white, micro-crystalline substance, m. p. 131°, is left; it contains nitrogen, and when heated with hydrochloric acid does not reduce Fehling's solution. When the decomposition of the nitrosochloride is effected under somewhat different conditions, a yellow, stable, crystalline substance, m. p. 53—54°, is obtained. The fractions of the oil, b. p. 178—179°, gave a crystalline *nitrosite*, m. p. 89—90°. The new terpene yields a dihydrochloride, m. p. 52°, identical with that of terpineol.

R. V. S.

#### Constitutional Formula of Crithmene. III. LUIGI

FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 382—386. Compare preceding abstract).—After reviewing the various formulae possible for this substance, the authors believe it to be  $\Delta^{1,7-4,8}$ -*p*-menthadiene (annexed formula). This constitution accords with the physical and chemical properties of the substance.

R. V. S.

**Depolymerisation and Transformation of Caoutchouc.** G. STAFFORD WHITHY (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 190—193. Compare this vol., i, 575).—It has been found that certain samples of

caoutchouc undergo a form of degenerative change in which the caoutchouc is converted into resin. During this process the original "tackiness" of the caoutchouc disappears, and the samples assume a smooth, polished appearance and become brittle. The extent to which the transformation occurs may be seen by the fact that a sample of such caoutchouc, which gave 9.9% of resin six weeks after collection, was found to contain 78% at the end of sixteen weeks.

The transformation is accompanied by increase in weight as a result of oxidation. A sample containing 19% of resin was found to have increased in weight to the extent of 4.38% at the end of three weeks. When kept in an air-bath at 100°, the increase in weight during the same period was 1.63%. The change goes on therefore at 100°, but at a slower rate. It is shown that the degenerative process has no connexion with the action of light, and that it is probably due to abnormal conditions, the origin of which must be sought for in the living plant. In this connexion, the function of the latex in the plant is obviously of primary importance, and in the later part of the paper the author puts forward the view that the latex represents a reserve supply of food which is rendered available by the action of an oxydase, and that the degenerative change of the extracted latex bears some relation to this oxidation process.

H. M. D.

#### Chemistry of Caoutchouc. III. Additive Compounds of Caoutchouc with Halogen Hydracids and Halogens.

FRIEDRICH W. HIRTSCHEN, HERMANN QUENSELL and ERICH KINDSCHER (*Ber.*, 1913, 46, 1283—1287).—Attempts have been made to obtain non-colloidal derivatives from caoutchouc, but without success. Cold benzene or chloroform solutions of pure Para caoutchouc have been saturated with hydrogen chloride, bromide or iodide, but the substances obtained on dilution with light petroleum still showed the Brownian movement when viewed in benzene solution under the ultra-microscope. The analyses were somewhat low for the *dihydrochloride*,  $C_{13}H_{10} \cdot 2HCl$ , a white powder, and the *dihydrobromide*, a white powder, which still retained bromine after boiling with alcoholic potassium hydroxide, whilst the *hydriodide*,  $C_{10}H_8 \cdot HI$ , was a colourless, sticky substance.

Chlorine in cold chloroform gave rise to substitution as well as addition, a white powder, which after repeated precipitation from alcohol gave numbers approximating to the formula  $C_{11}H_{14}Cl_3$  (compare Gladstone and Hibbert, *T.*, 1888, 53, 679). The bromination of caoutchouc in ice-cold chloroform is practically independent of the amount of bromine used or of the time, and leads to the tetrabromide. The application of the process to the estimation of caoutchouc will be published later.

J. C. W.

#### Chemistry of Caoutchouc. IV. Action of Iodine on Caoutchouc.

FRIEDRICH W. HIRTSCHEN and RICHARD KEMPF (*Ber.*, 1913, 46, 1287—1291).—Weber (*A.*, 1900, i, 354) described a compound,  $C_{20}H_{22}I_2$ , which he obtained by the action of iodine on caoutchouc in cold chloroform. Such a great absorption of iodine could not be obtained in the present experiments, but it is found that

the process is a photochemical reaction, and, as such, is almost independent of temperature. Small portions of a 1% solution of iodine were quickly rendered colourless in sunlight on addition to a 1% solution of caoutchouc in carbon disulphide, when the end-point corresponded with the absorption of one atom of iodine by two molecules of hydrocarbon. A specific action of short-waved light could not be determined, but the volume of air over the liquid seemed to be of importance. On filtering the bleached and somewhat evaporated solution into light petroleum, a white powder was obtained which approximated to the formula  $C_{30}H_{27}O_2I$ . It gave up iodine when kept, but in an iodine atmosphere in the dark it rapidly absorbed the halogen, and after three weeks had increased in weight by 170%. The glistening black product approximated therefore to  $C_{30}H_{27}O_2I_3$ . J. C. W.

**Chemistry of Caoutchouc. V. Treatment of Caoutchouc with Sulphur Chloride and Sulphur.** FRIEDRICH W. HINRICHSSEN and ERICH KINDSCHER (*Ber.*, 1913, 46, 1291—1297. Compare A., 1910, i, 330).—The cold vulcanisation of caoutchouc was studied by mixing a constant weight of caoutchouc in dry benzene with varying amounts of sulphur chloride and, after some time, measuring the excess of reagent. The end-product was found to agree with the formula  $(C_{10}H_{10})_2S_2Cl_2$ . The action of sulphur was first studied in naphthalene solution, but now systematic experiments have been carried out at 170° in cumene. The product is repeatedly extracted with acetone, when the resulting hard, brown powder is found to contain a proportion of sulphur which approaches to 32% more and more as the initial concentration of sulphur and the time of heating are increased. This corresponds with  $C_{10}H_{10}S_2$  (compare Spence and Young, A., 1912, i, 706), and since the substance does not absorb bromine it is regarded as a definite compound. If the uncombined sulphur is extracted by alcoholic sodium hydroxide, however, the product contains less than 26% of sulphur. J. C. W.

**Vulcanisation of Caoutchouc. II.** GUSTAV BERNSTEIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 193—196. Compare A., 1912, i, 1006).—The "depolymerisation" of caoutchouc under the influence of a rise of temperature, mechanical treatment, and ultra-violet light has been investigated by measurements of the viscosity of xylene solutions of the caoutchouc. Samples of caoutchouc which in xylene solution show widely different viscosities are found to give the same value for the viscosity when subjected to the depolymerising action of heat, light or mechanical treatment until the viscosity has become constant. This result would seem to show that the state of aggregation which is finally attained is independent of the special characteristics of the original caoutchouc.

From measurements of the viscosity of xylene solutions of Hevea Plantation caoutchouc which was heated for five hours at temperatures between 50° and 100°, it has been found that rapid depolymerisation begins at 60—70°. This temperature was found to vary somewhat when caoutchoucs from other sources were examined in the same way.

If sulphur is mixed with the caoutchouc before exposure to ultra-violet light, it is found that vulcanisation takes place as a result of the light treatment. Vulcanisation also occurs when a xylene solution containing caoutchouc and sulphur is exposed to the short-waved rays.

H. M. D.

**Synthetic  $\beta$ -Glucosides of the Terpene Alcohols.** JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, 50, 209—219).—By the method already described (this vol., i, 497), the following substances were prepared. *Sabinol-tetra-acetyl-d-glucoside*,  $C_{24}H_{34}O_{16}$ , long, glistening needles, m. p.  $121^\circ$  (corr.). *Sabinol-glucoside*,  $C_{16}H_{26}O_{10}$ , m. p.  $65-68^\circ$  (corr.),  $[\alpha]_D^{20}$  of anhydrous substance  $-33.60^\circ$ . This glucoside is hydrolysed by emulsin. *d-Camphenol-tetra-acetyl-d-glucoside*,



long, glistening needles, m. p.  $128.5-130^\circ$  (corr.). *d-Camphenol-d-glucoside*,  $C_{16}H_{26}O_{10}$ , m. p.  $95-98^\circ$  (corr.),  $[\alpha]_D^{20}$  of anhydrous substance  $-25.47^\circ$ . This is slowly hydrolysed by emulsin. *1-Fenchyl-tetra-acetyl-d-glucoside*,  $C_{24}H_{36}O_{16}$ , m. p.  $119-121.5^\circ$  (corr.). *1-Fenchyl-d-glucoside*,  $C_{16}H_{28}O_{10}$ , with  $[\alpha]_D^{20} -36.57^\circ$ . The substance with water of crystallisation has m. p.  $124-127^\circ$  (corr.), m. p. of anhydrous glucoside  $130-132.5^\circ$  (corr.), sinters at  $122^\circ$ . It is slowly hydrolysed by emulsin. *r-Borneol-tetra-acetyl-d-glucoside*,  $C_{24}H_{36}O_{16}$ , m. p.  $119.5-122.5^\circ$  (corr.). *r-Borneol-d-glucoside*,  $C_{16}H_{28}O_{10}$ , with  $[\alpha]_D^{20} -32.99^\circ$ , m. p. of substance with water of crystallisation  $133-134.5^\circ$  (corr.), and of anhydrous substance  $143-144.5^\circ$  (corr.), sinters at  $132^\circ$ . It is very slowly hydrolysed by emulsin. *l-Borneol-tetra-acetyl-d-glucoside*,  $C_{24}H_{36}O_{16}$ , m. p.  $124^\circ$  (corr.). *l-Borneol-d-glucoside*,  $C_{16}H_{28}O_{10}$ , m. p.  $132.5-133.5^\circ$  (corr.). The anhydrous substance has m. p.  $138-141^\circ$  (corr.), and  $[\alpha]_D^{20} -60.12^\circ$ . It is fairly readily hydrolysed by emulsin.

S. B. S.

**Helleborein.** ERNST SIEBURG (*Arch. Pharm.*, 1913, 251, 154—183. Compare Thaeter, A., 1898, i, 39).—Helleborein is shown to belong to the group of saponins. On hydrolysis it yields: acetic acid, dextrose, arabinose, and two sapogenins called "acid" and "neutral" helleboretin respectively, which are closely related and probably contain a terpene-like nucleus. As the result of pharmacological experiments, the author suggests that helleborein is not a suitable substitute for digitalin in medicine.

Helleborein (Merck),  $(C_{21}H_{34}O_{10})_2$ ,  $[\alpha]_D^{20} -2.8^\circ$ , is amorphous; it furnishes an acetyl derivative,  $(C_{21}H_{32}O_{10}Ac)_2$ , m. p.  $129-130^\circ$ , which separates from alcohol in yellow scales, and on treatment with baryta yields a product, which is helleborein less one acetyl group (see below), and forms a pale yellow powder. *Benzoylhelleborein*,  $(C_{21}H_{32}O_{10}Bz)_2$ , m. p.  $142^\circ$ , is a snow-white, amorphous substance. When boiled with baryta solution, helleborein loses one molecule of acetic acid, and the latter acid is also formed when the glucoside is treated with bromine water. On hydrolysis, by boiling with dilute sulphuric acid, 1 mol. of acetic acid and 2 mols. each of dextrose and arabinose are formed. The other products of hydrolysis are *acid helleboretin* and *neutral helleboretin*. The former has the formula  $C_{21}H_{32}O_7$ , and appears to be a lactone, since it does not decompose carbonates and is not completely

soluble in alkali hydroxide solutions. Its behaviour on treatment with melted potassium hydroxide or nitric acid, and on distillation with zinc dust is recorded. Neutral helleboretin,  $C_{15}H_{24}O_8$ , is a greenish-black mass. The deacetylated helleborein referred to above does not produce hemolysis, and is not poisonous to rabbits.

T. A. H.

**Structure of the Natural Saponins.** ANNE W. VAN DER HAAR (*Arch. Pharm.*, 1913, 251, 217—223. Compare A., 1912, i, 885).—The method of investigation previously described (*loc. cit.*) has been applied to guaiacum-saponin, saponin and sapotoxin from *Levantine saponaria* root, senegin and digitonin, and it is shown that all five of these saponins give the characteristic colour reaction with sulphuric acid. Further, the saponogenins obtained from them by acid hydrolysis, on distillation with zinc dust, yield products which can be separated by steam distillation into terpene-like oils and non-volatile products. The terpene-like oils give a violet coloration with acetic acid and sulphuric acid, whilst the non-volatile substances give the blue (phytosterol) reaction with this reagent. In the case of the products from the saponin derived from senegin, these colour reactions are, however, reversed.

T. A. H.

**Strophanthic Acid, a Saponin from the Seeds of *Strophanthus Gratus*.** ERNST SIEBURG (*Ber. Deut. pharm. Ges.*, 1913, 23, 278—290).—The different varieties of *Strophanthus* do not contain more than 0.2% of strophanthic acid.

The mother liquors obtained in the manufacture of *g*-strophanthin formed the starting material for the isolation of the acid. They were neutralised, diluted with water, freed from fat, and acidified with hydrochloric acid. The crude precipitated acid was repeatedly washed with water, and then precipitated with basic acid acetate; the precipitate was washed with water, and extracted with boiling 80% alcohol; the extract was diluted with water and shaken with isobutyl alcohol; from its solution in the latter medium, *g*-strophanthic acid was precipitated by addition of ether as a white, amorphous, voluminous mass, which was acid towards litmus, and readily dissolved in aqueous alkali carbonate and hydrogen carbonate solutions.

*g*-Strophanthic acid is precipitated from its aqueous solution by phosphotungstic, phosphomolybdic, and picric acids, but not by tannin. It has only feeble reducing action towards the ordinary reagents. It does not contain a methoxy-group. It yields precipitates with the salts of many heavy metals, such as copper, lead, zinc, ferrous and ferric iron, and barium, but the products do not appear to be definite chemical individuals. The solubility of the free acid appears to depend somewhat on the age of the specimens. Ultimate analysis, titration with sodium hydroxide, and analysis of the silver and lithium salts lead to the formula  $C_{21}H_{34}O_{10}$  for the acid, but determination of molecular weight in glacial acetic acid solution indicates the formula  $(C_{21}H_{34}O_{10})_4$ .

When hydrolysed with 3% aqueous sulphuric acid, and subsequently with 4% alcoholic hydrochloric acid, strophanthic acid yields dextrose and *strophanthigenin*,  $(C_{12}H_{18}O_2)_2 \cdot 3\frac{1}{2}H_2O$ , white needles, m. p. about

294°. The latter is faintly acidic in solution, but does not dissolve even in concentrated alkali. With bromine in glacial acetic acid solution, it yields an uncrystallisable product,  $C_{12}H_{18}Br_2O_2$ . Oxidation with potassium permanganate converts it into a crystalline acid, which has not been further investigated.

The following colour reactions are shown by *g*-strophanthic acid, and generally with greater readiness by *g*-strophanthigenin, but are not given by *k*-strophanthin, *g*-strophanthin, or *g*-strophanthidin: (1) a trace of substance gives an immediate yellowish-red coloration, with concentrated sulphuric acid, which gradually changes to an eschewer red with greenish fluorescence; (2) if a dilute solution of the substance in alcohol is mixed with an alcoholic solution of benzaldehyde and evaporated, the residue gives an immediate bright red coloration with sulphuric acid; (3) if a trace of the substance is dissolved in acetic anhydride and concentrated sulphuric acid cautiously added, a red ring is formed which rapidly becomes violet, then blue, and finally green; (4) a saturated alcoholic solution of dextrose or arabinose yields with a trace of substance and concentrated sulphuric acid a red ring which quickly turns to violet; with furfuraldehyde, under like conditions, a blue to green colour is developed; (5) if rhamnose is used, as in (4), a permanent, deep cherry-red colour is formed; (6) a solution of the substance in a mixture of nine parts trichloroacetic acid and one part concentrated hydrochloric acid gradually develops a pale violet colour, which becomes more intense and slightly fluorescent. H. W.

**Thiophen Analogues of Triphenylethyl.** MOSES GOMBERG and R. L. JICKLING (*J. Amer. Chem. Soc.*, 1913, 35, 446—447).—Attempts have been made to prepare analogues of triphenylmethyl containing other than exclusively aromatic groups.

*Thienyldiphenylcarbinyl chloride* has m. p. 81°; when a solution in benzene is treated with molecular silver, it becomes dark red, and an unsaturated hydrocarbon is produced which absorbs oxygen with formation of the peroxide  $(C_6SH_5 \cdot CPh_2)_2O_2$ .

*Dithienylphenylcarbinol*, m. p. 90°, has been prepared by the Grignard synthesis from ethyl benzoate and thienyl chloride. E. G.

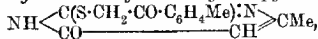
**1:4-Dithiens.** TREAT B. JOHNSON, ROBERT C. MORAN, and EDWARD F. KOHMANN (*J. Amer. Chem. Soc.*, 1913, 35, 447—452).—Johnson and Moran (*A.*, 1912, i, 913) have found that when 2-benzoylmethylthiol-4-methyl-1:6-dihydro-6-pyrimidone is hydrolysed with concentrated hydrochloric acid, it yields 4-methyluracil together with a crystalline compound containing sulphur. A study of the latter compound has shown that it has the structure  $S < \begin{smallmatrix} CPh_2CH \\ CH:CPh_2 \end{smallmatrix} > S$ , and it has therefore been designated 2:5-diphenyl-1:4-dithien. Both this substance and the corresponding 2:5-ditolyl compound are yellow, but dissolve in concentrated sulphuric acid to form beautiful purple solutions. Characteristic colorations are also produced by strong nitric acid and by solution of bromine in glacial acetic acid. In this respect the dithiens resemble Fries and Volk's thianthren compounds (*A.*, 1909, i, 406). 1:4-Dithien, the parent substance of the compounds now



described, has been obtained by Levi and termed by him biophen (A., 1891, 551).

2:5-Diphenyl-1:4-dithien, m. p. 118—119°, crystallises in yellow prisms and is exceedingly stable.

2-p-Toluylmethylthiol 4-methyl-1:6-dihydro-6-pyrimidone,



m. p. 194—195°, obtained by the action of *p*-chloroacetyl toluene on the sodium salt of 2-thio-4-methyluracil, forms colourless, prismatic crystals. On hydrolysis with 20% hydrochloric acid, it yields 2:5-diphenyl-1:4-dithien, m. p. 137—138°, which crystallises in yellow needles.

E. G.

The Hellebore Group. III. Alkaloids of Delphinium Ajacis. OSKAR KELLER and O. VÖLKER (*Arch. Pharm.*, 1913, 251, 207—216, Compare A., 1910, ii, 887, 888).—This plant yields two new alkaloids, which are characterised.

The alkaloids were isolated from an alcoholic extract of the seeds. *Ajacine*,  $\text{C}_{15}\text{H}_{21}\text{O}_4\text{N}\cdot\text{H}_2\text{O}$ , m. p. 142—143°, crystallises in colourless needles from dilute alcohol, is alkaline in reaction, and yields salts which are readily soluble and difficult to crystallise. The *hydrochloride*,  $\text{B}_2\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ , m. p. 93°, is amorphous, as is also the *aurichloride*,  $\text{B}_2\cdot\text{HAuCl}_4$ , and the *platinichloride*,  $\text{B}_4\cdot\text{H}_2\text{PtCl}_6$ . The alkaloid absorbs bromine, contains 3 methoxyl groups, is not esterified by benzoyl chloride or acetic anhydride, does not react with methyl iodide or methyl sulphate, and is not affected by nitrous acid. On oxidation, it furnished a product smelling of butyric or valeric acid, and on distillation with zinc dust yielded a substance having an odour of benzaldehyde. On treatment with cyanogen bromide, it furnished a crystalline compound, m. p. 132—133°.

*Ajaconine*, m. p. 162—163°, forms colourless, glancing prisms, but concordant results could not be obtained on combustion, and crystalline salts could not be prepared. It contains no methoxyl groups. With methyl iodide, a crystalline *methiodide*, m. p. 121°, slender needles, was obtained, which appears to have the formula  $\text{C}_{18}\text{H}_{31}\text{O}_2\text{N}\cdot\text{HI}\cdot\text{H}_2\text{O}$ , whence the formula  $\text{C}_{17}\text{H}_{29}\text{O}_2\text{N}$  is assigned provisionally to the parent base. The latter may be a secondary base, since it reacts with nitrous acid, forming a substance which gives Liebermann's reaction. *Ajaconine* also yields an amorphous *di-benzoyl* derivative, from which an amorphous *aurichloride* was prepared.

The behaviour of both alkaloids with the usual precipitants and reagents is described. The seeds also contain other alkaloids, which are amorphous.

T. A. H.

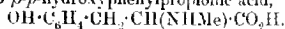
Comparative Solubility of Morphine and Narcotine in Pure or Aqueous Acetone and in Distilled Water. GABRIEL GÉRARD (*J. Pharm. Chim.*, 1913, [vii], 7, 436).—One litre of pure anhydrous acetone dissolves at 15°, 1.28 grams of morphine and 41.96 grams of narcotine. In a mixture of equal volumes of acetone and water at 15°, the solubilities are morphine 1.32 grams, and narcotine 0.70 gram

per litre. In distilled water at 15°, the solubilities are morphine, 0.288 gram, and narcotine, 0.10 gram per litre. W. P. S.

*apo*Morphine. I. Supposed Formation of *apo*Morphine on Heating or Keeping Morphine Solutions. MORITZ FEINBERG (*Zeitsch. physiol. Chem.*, 1913, 84, 363—378).—*apo*Morphine is not formed either on prolonged boiling of morphine, morphine hydrochloride, or liquids containing morphine, such as pantopone, or on keeping such solutions with or without the addition of a nutrient substance. The separations occasionally observed from such solutions are due to traces of the sparingly soluble morphine base. Preparations of *apomorphine* obtained in commerce had the theoretical proportion of chlorine, and agreed as to their optical activity. They are therefore to be regarded as pure. E. F. A.

The Polymorphism of Codeine, Thebaine, and Narcotine; a New Type of Spherulites. PAUL GAUBERT (*Compt. rend.*, 1913, 156, 1161—1163).—Codeine, thebaine and narcotine, and other alkaloids derived from opium, exhibit the phenomenon of superfusion, become solid without crystallisation, and can be kept in this vitreous state for several months. They are all polymorphic, codeine having five crystalline forms, narcotine three, and thebaine two, varying in stability with the temperature, and they also all present curious spherulitic formations at different temperatures. W. G.

The Structure of Ratanhine. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1913, 34, 659—664. Compare this vol., i, 71).—The estimation of methyl attached to nitrogen in ratanhine indicates the presence of a methylamino-group in this substance, and it is therefore possible that ratanhine is  $\alpha$ -methylamino- $\beta$ -*p*-hydroxyphenylpropionic acid (methyl-tyrosine). The m. p. is so indefinite that it is of little use as a comparison with the synthetical substance of this structure (Johnson and Nicolet, A., 1912, i, 585), but the action of iodine on alkaline solutions of ratanhine and of the synthetic substance produces apparently the same di-iodo-compound from each. The probability of the above structure for ratanhine is strongly confirmed by the close resemblance of the base, which is obtained by scission of carbon dioxide, with  $\beta$ -*p*-hydroxyphenylethylmethylamine (Walpole, T., 1910, 97, 945); the free bases, together with the hydrochlorides and platinumchlorides, exhibit a close agreement in m. p. It is therefore to be accepted that ratanhine, which is also known by the names suinamine (Blau, A., 1909, i, 51), geoffroyine, angeline, and andinine, is  $\alpha$ -methylamino- $\beta$ -*p*-hydroxyphenylpropionic acid,



D. F. T.

Synthesis of 2:3:4-Trimethylpyrrole and of 2:3:4-Trimethyl-5-ethylpyrrole (Isomeric Phyllopyrroles). HANS FISCHER and AMANDUS HANS (*Zeitsch. physiol. Chem.*, 1913, 84, 254—261).—Fischer and Kroll-Feiffer (this vol., i, 93) have described the formation of the phthalide of a trimethylpyrrole by treating tetramethylpyrrole with phthalic anhydride. Potassium hydroxide

converts this phthalide into the corresponding acid, which after prolonged treatment with glacial acetic acid and hydrogen iodide loses the phthalic acid residue and forms 2:3:4-trimethylpyrrole, described by Piloty and Hirsch (*A.*, 1912, i, 925). This alkylpyrrole has marked crystallising properties; it forms a crystalline picrate and an azo-dye, and is oxidised by nitrous acid to an oxime, which is converted into dimethylmaleinimide on hydrolysis.

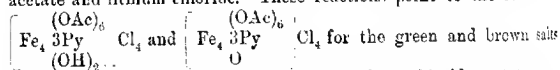
Heating with sodium ethoxide converts the trimethylpyrrole into the isomeric phyllopyrrole, which does not crystallise.

Tetramethylpyrrole is produced when the above phthalide is heated with sodium methoxide.

On heating indigotin with sodium methoxide in sealed tubes at 236°, the C-C-junction is broken, and dimethylindole is formed as well as a second unknown compound, which crystallises well and forms a picrate, m. p. 176—177°.

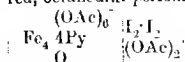
3:4:5-Trimethylpyrrole crystallises in prisms, m. p. 37—38°, becoming red when exposed to the air. The picrate has m. p. 147—148°.  
E. F. A.

**Complex Acetatoferri-bases Containing Pyridine.** RUDOLF F. WEINLAND and CHR. BECK (*Zeitsch. anorg. Chem.*, 1913, 80, 402—447. Compare *A.*, 1910, i, 296, 635).—When pyridine (5 mols.) is added to a solution of hydrated ferric chloride (1 mol.) in glacial acetic acid (5 mols.), heat is developed and a dark green mass is obtained on cooling. When this is dissolved in chloroform and precipitated with benzene, yellowish-green crystals are obtained. Digestion with absolute alcohol converts this salt, with loss of water, into a brown, octahedral salt, and an exactly similar salt is obtained from ferric bromide. The original chloride yields a yellowish-green iodide with concentrated aqueous potassium iodide, the chlorine being completely eliminated, whilst the chloride is regenerated from the acetate and lithium chloride. These reactions point to the formulae.



The original crude product is a chloride-acetate, containing more pyridine. The brown solutions of these salts in water slowly decompose, forming a gelatinous precipitate. Benzene does not precipitate a pure tetrabromide from chloroform solution, but a mixed salt containing more pyridine. Removal of water gives a salt corresponding exactly with the chloride.

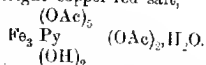
A solution of ferric acetate and lithium iodide in glacial acetic acid yields an iodide-acetate, composed of two mixed salts. Digestion with absolute alcohol yields a red, octahedral periodide-acetate,



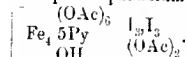
The iodide obtained from the chloride is a mixed salt. Nitrate acetate have also been obtained.

Ferric acetate, pyridine, and glacial acetic acid yield a compound

$$\text{Fe}_4 \left[ \begin{array}{c} (\text{OAc})_6 \\ 3\text{Py} \\ \text{OH} \end{array} \right] (\text{OAc})_6.$$
 Dissolving in chloroform and precipitating with benzene gives a bright copper-red salt,



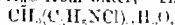
Solutions of ferric chloride in at least 15 mols. glacial acetic acid yield after a time with 2 mols. of pyridine, garnet-red prisms, which contain more chlorine than the previous salts, and appear to contain a complex anion,  $\left[ \text{Fe} \begin{array}{c} \text{Cl}_3 \\ \text{H}_2\text{O} \end{array} \right]$ , which is already known. The salt is acid and is only stable in presence of an excess of acetic acid. It has the constitution  $\left[ \text{Fe}_4 \begin{array}{c} (\text{OAc})_6 \\ 5\text{Py} \\ \text{OH} \end{array} \right] \left[ \text{Fe} \begin{array}{c} \text{Cl}_3 \\ \text{H}_2\text{O} \end{array} \right]_2 (\text{OAc})_2 \cdot \text{CH}_3 \cdot \text{CO}_2\text{H} \cdot 12\text{H}_2\text{O}$ . It yields a periodide with concentrated aqueous potassium iodide,



The iron atoms in the complex cations are regarded as linked together through the acetyl groups by means of subsidiary valencies. The pyridine in these compounds, like the ammonia in the complex chromiactates, can pass in and out of the cation without, as in metal-ammines, affecting the negative groups. C. H. D.

**Pyridine Derivatives.** ERNST SCHMIDT (*Arch. Pharm.*, 1913, 251, 183—207).—In continuation of work already described (A., 1905, i, 23), attempts have been made to prepare formocholine (trimethylhydroxymethylammonium hydroxide), and in default of this its pyridine analogue, by new methods which will give larger yields. The products obtained in these unsuccessful attempts are described.

Prescott and Baer (A., 1897, i, 95) have shown that by the interaction of methylene iodide and pyridine, methylenedipyridyl iodide,  $\text{CH}_2(\text{C}_5\text{H}_5\text{NI})_2$ , is formed, and a further study of this reaction under various conditions shows that this is practically the sole product. It forms yellow leaflets, m. p. 220° (decomp.), but after decolorization by animal charcoal forms colourless tablets, m. p. 222—223°, containing 1  $\text{H}_2\text{O}$  from water. The chloride,



is similar, but remains unmelted at 260°. The *platinichloride* forms yellow needles from alcohol, and does not melt at 260°. The *picrate* forms long, yellow needles, m. p. 230°, and the *mercurichloride*,  $\text{CH}_2\text{C}(\text{H})_2\text{NCl}_2 \cdot 4\text{HgCl}_2$ , long, glancing needles, m. p. 230°; the mother liquor from the preparation of the latter salt deposits on evaporation a second *mercurichloride*, m. p. 121—126°, containing 1 mol.  $\text{HgCl}_2$ .

Attempts to demethylate pyridylformocholine methyl ether (A., 1901, i, 413) by L. KRATZ furnished only pyridine.

Re-examination of Prescott and Baer's work (*loc. cit.*) on the interaction of ethylene bromide and pyridine shows that in addition

to ethylenedipyridyl bromide some bromoethylpyridyl bromide (*platinichloride*,  $[C_5H_5NCl \cdot C_2H_4Br]_2 \cdot PtCl_4$ , long needles, m. p. 229°) is formed. In isolating the substance, the mother liquors were treated with platinic chloride, and in this way the following double *platinichlorides* and *aurichlorides* with pyridino were obtained.

(1).  $[C_5H_5N, HCl]_2 \cdot PtCl_4 + [C_5H_5NCl \cdot C_2H_4Cl]_2 \cdot PtCl_4$ , reddish-yellow leaflets, m. p. 195°;  $C_5H_5N, HAuCl_4 + C_5H_5NCl \cdot C_2H_4Cl, AuCl_3$ , glancing needles, m. p. 142—143°.

(2).  $[C_5H_5N, HCl]_2 \cdot PtCl_4 + C_5H_5NCl \cdot C_2H_4Cl, PtCl_4$ , yellowish-brown, nodular crystals, m. p. 180—181°; the corresponding *aurichloride* formed leaflets, m. p. 155°.

*Ethylenedipyridyl chloride*,  $C_2H_4[C_5H_5NCl]_2$ , obtained by treating the bromide with silver chloride in water or by the direct action of ethylene chloride on pyridine, crystallises in leaflets or tablets, both forms containing alcohol of crystallisation, and does not melt at 260°. The *aurichloride*,  $1.2AuCl_3$ , forms small, leafy crystals from dilute alcohol. The *picrate*, m. p. 246°, forms yellow leaflets. *Chloroethylpyridyl chloride* is a hygroscopic, syrupy mass; the *platinichloride*, m. p. 218° (decomp.), forms needles, and the *aurichloride*, m. p. 135—136°, needles or leaflets, from water.

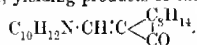
[With A. SEEBERG.]—On heating bromoethylpyridyl bromide with silver nitrate in aqueous solution, pyridinecholme is produced. This yields an *aurichloride*, m. p. 117°, crystallising in broad needles or leaflets, a *platinichloride*, m. p. 179°, forming reddish-yellow tablets, and a *mercurichloride*, m. p. 188—189°, as a colourless, crystalline powder (compare Roitner, A., 1895, i, 319, and Litterscheid, A., 1902, i, 308).

When silver oxide is used the product is pyridineurine, which yields an *aurichloride*, m. p. 178°, crystallising in long, yellow needles, and a *platinichloride*, m. p. 193° (decomp.), forming small tablets.

T. A. H.

**Kynurenic Acid.** (Miss) ANNIE HOMER (*Proc. Physiol. Soc.*, 1913, xviii; *J. Physiol.*, 46).—The kynurenic acid of dog's urine is 2-hydroxyquinoline-4-carboxylic acid. It has m. p. 288—289°; this is a higher figure than that given by previous workers. W. D. H.

The Ten Stereoisomeric Tetrahydroquinaldinomethylene-camphors. WILLIAM J. POPE and JOHN READ (*Proc. Camb. Phil. Soc.*, 1913, 17, [2], 201).—The two enantiomorphously related tetrahydroquinaldines condense readily with the two similarly related oxymethylenecamphors, yielding products of the constitution



Since each component of the condensation can be obtained in a dextro- and a levo-rotatory form, four simple optically active condensation products can be obtained, represented by the configurations: (1) *d-d*, (2) *l-l*, (3) *d-L*, (4) *l-D* (*d* and *l* represent the configurations of the tetrahydroquinaldine residue, and *D* and *L* those of the oxymethylene-campher nucleus). From these the two racemic compounds (5) [*d-D*, *l-L*] and (6) [*d-L*, *l-D*] can be prepared, whilst in the present

instance the following two pairs of partly racemic compounds are also obtainable: (7) [*d*-*D*, *d*-*L*], (8) [*l*-*L*, *l*-*D*], (9) [*d*-*D*, *l*-*D*], and (10) [*l*-*L*, *d*-*L*].

It would be anticipated that no resolution of externally compensated tetrahydroquinaldine into its optically active components would be possible with the aid of *d*- or *l*-oxymethylenecamphor. It is shown, however, that on treating externally compensated tetrahydroquinaldine with less than one-half an equivalent of *d*-oxymethylenecamphor, a resolution can be effected because the *l*-base condenses more rapidly than the *d*-isomeride with *d*-oxymethylenecamphor; under these conditions the condensation yields about 80% of the partly racemic compound (9) and 20% of the optically active substance (4), from which *l*-tetrahydroquinaldine may be separated.

H. W.

**Preparation of Hydroxycarbazole.** FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 258298. Compare A., 1907, i, 1074; T., 1911, 99, 103).—*Carbazoletrisulphonic acid* is obtained when carbazole (3 parts) dissolved in concentrated sulphuric acid (10 parts) is gently warmed with 3 parts of fuming sulphuric acid (20% SO<sub>3</sub>).

*Potassium carbazotrisulphonate* forms colourless crystals, and when fused with potassium hydroxide (3 parts), first at 190–200° and subsequently at 220–230°, furnishes the crystalline *potassium hydroxycarbazotrisulphonate*.

*1-Hydroxycarbazole* (annexed formula), colourless leaflets, m. p. 163°, is obtained when the foregoing potassium hydroxycarbazole disulphonate is heated with 5% sulphuric acid during five hours at 180°, and is not identical with the hydroxycarbazole (m. p. 255–256°) prepared by Ruff and Stein (A., 1901, i, 620).

F. M. G. M.

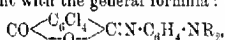
**Action of Formic Acid on Triphenylmethane Dyes.** ALFRED GUYOT and A. KOVACHE (*Compt. rend.*, 1913, 156, 1324–1327. Compare A., 1912, i, 186, 972).—Hexamethyl-violet and malachite-green are only very slightly reduced by pure formic acid. The addition of sodium formate, however, causes rapid reduction with the evolution of carbon dioxide, which takes place in two stages, the second requiring the presence of a large amount of formate. The hexamethyl-violet is first reduced like the simple triarylcannabinols (*loc. cit.*), and gives hexamethyltriaminotriphenylmethane, which then undergoes further reduction to dimethylaniline and tetramethyl-*p*-diaminodiphenylmethane, with the evolution of a second molecule of carbon dioxide. This reduction is quantitative, whereas with malachite-green the reduction, whilst proceeding similarly, is never quantitative in the second stage. The authors consider that this action of formic acid establishes evident relationship and a complete continuity between the dyes proper and the cannabinols deprived of all auxochrome; between these two groups there only exists a difference in reactional aptitude, which can be attributed to the more or less pronounced basicity of the molecules, and which shows itself in the varying ease with which reduction takes place from one member to another.

W. G.

**Tetrachlororhodamines.** MARCEL BLOCH (*Bull. Soc. ind. Mulhouse*, 1913, 83, 81--84).—When an equimolecular mixture of *m*-dimethylaminophenol and tetrachlorophthalic anhydride is heated at 165°, *tetramethyltetrachlororhodamine phthalate* is obtained, which, by the successive action of sodium hydroxide and hydrochloric acid, is converted into the corresponding *hydrochloride*, green crystals, from which the free base is obtained by addition of sodium hydroxide. The latter dyes cotton, wool, and silk in reddish-violet shades exhibiting, in the case of the latter fibre, a magnificent fluorescence. The colours are stable towards light and alkalis. Attempts to esterify the rhodamine were unsuccessful, probably owing to the presence of electronegative atoms in the ortho-position to the carboxyl group.

When *m*-dimethylaminophenol is heated with tetrachlorophthalic anhydride in xylene solution, *o*-4-dimethylamino-2-hydroxybenzoyltetrachlorobenzoic acid,  $\text{NMe}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{Cl}_4\cdot\text{CO}_2\text{H}$ , is formed together with a substance, separating from glacial acetic acid in yellow needles, which probably has the formula  $\text{C}_6\text{Cl}_4(\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ .

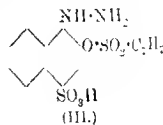
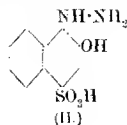
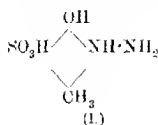
By the condensation of tetrachlorophthalic anhydride with *m*- or *p*-phenylenediamine or their alkylated derivatives in glacial acetic acid solution, a series of yellow compounds has been prepared which yield colourless salts with hydrochloric acid. Results of analyses are in agreement with the general formula:

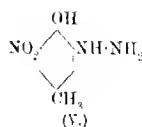
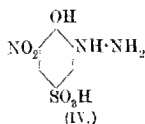


*Tetrachlororhodamine* (annexed formula) is formed by the condensation of 4-dimethylamino-2-hydroxy-*o*-benzoyltetrachlorobenzoic acid with *p*-cresol in the presence of concentrated sulphuric acid, whilst with resorcinol or pyrogallol the same acid yields substituted rhodols.

H. W.

[Preparation of Hydroxyphenylhydrazinesulphonic Acids and their Condensation Products] FARHWERK MÜLLHEIM VON A. LEONHARDT & Co. (D.R.-P. 258017).—When the *o*-hydroxyphenylhydrazines are condensed with *o*-diketones they give rise to dyes, and the preparation of the following substituted hydrazines by diazotisation and reduction of the corresponding bases is described: 4-hydroxy-*m*-tolylhydrazine-5-sulphonic acid (I); 2-hydroxy-1-naphthylhydrazine-4-sulphonic acid (II), and its tolylsulphonyl ester (III); 5-nitro-2-hydroxyphenylhydrazine-5-sulphonic acid (IV), and 5-nitro-4-hydroxy-*m*-tolylhydrazine (V), whilst the tinctorial properties of the compounds obtained by condensing them with camphorquinone, phenanthraquinone, and other *o*-diketones are tabulated in the original.





F. M. G. M.

**Hydrazones of Hydroxy-aldehydes and ketones; Alkali-insoluble Naphthols.** HENRY A. TORREY and CARL M. BREWSTER (*J. Amer. Chem. Soc.*, 1913, **35**, 426—444).—Torrey and Kipper (A., 1907, i, 325; 1908, i, 460) have shown that the insolubility of certain phenols in aqueous alkali hydroxides depends (1) on the hydroxyl group being in the ortho-position to a large side-chain, and (2) on the other substituting groups in the benzene nucleus to which the hydroxyl group is attached. In the present paper an account is given of certain naphthol derivatives which are insoluble in alkali hydroxide solutions.

The naphthalene group,  $\begin{smallmatrix} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix}$ , is more effective in producing insolubility than any other group yet studied. There does not seem to be any marked difference between the derivatives of 1-hydroxy- $\beta$ -naphthyl methyl ketone (2 acetyl-1-naphthol) and naphthaldehyde; the phenylhydrazones, *p*-bromophenylhydrazones, phenylbenzylhydrazones,  $\alpha$ - or  $\beta$ -naphthylhydrazones, and the benzidine compounds of both substances show the same insolubility.

The following compounds of 1-hydroxy- $\beta$ -naphthyl methyl ketone are described. The  $\alpha$ -naphthylhydrazone,  $\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{CMe} : \text{N} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , m. p. 179—180°, insoluble in boiling aqueous sodium hydroxide; the  $\beta$ -naphthylhydrazone, m. p. 174—176°, insoluble in warm 10% sodium hydroxide; the phenylbenzylhydrazone, m. p. 150—152°, insoluble in boiling 10% sodium hydroxide; the *azine*, which decomposes at a high temperature and is insoluble in warm 10% sodium hydroxide, and its acetate, m. p. 169—170°; the benzidine compound,

$\text{C}_{12}\text{H}_8(\text{N} : \text{CMe} \cdot \text{C}_{10}\text{H}_7 \cdot \text{OH})_2$ , decomposing at 210°, and insoluble in boiling 10% and 30% sodium hydroxide; the semicarbazone, m. p. 245—250°, easily soluble in cold aqueous sodium hydroxide; the  $\beta$ -naphthylimide,

$\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{CMe} : \text{N} \cdot \text{C}_{10}\text{H}_7$ , m. p. 161—162°, insoluble in boiling 10% sodium hydroxide; and the *p*-aminophenol compound,  $\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{CMe} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , which decomposes at 210—220° and is easily soluble in cold aqueous sodium hydroxide.

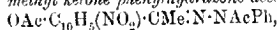
1:5-Diphenyl-3- $\alpha$ -naphtholpyrazoline,  $\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{C}_5\text{H}_4\text{N}_2\text{Ph}_2$ , m. p. 180° (decomp.), prepared by the action of phenylhydrazine on 2-benzylideneacetyl-1-naphthol (Kostanecki, A., 1898, i, 373), is insoluble in boiling 10% and 30% aqueous sodium hydroxide.

Promo-1-hydroxy- $\beta$ -naphthyl methyl ketone,  $\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{Br} \cdot \text{COMe}$ , has been described in an earlier paper (Torrey and Brewster, A., 1910, i, 48). The *acetyl* derivative, m. p. 95—96°, is insoluble in cold sodium hydroxide solution, but gradually decomposes on warming; the



*a*-naphthylhydrazone, m. p. 175—176° (decomp.), is insoluble in boiling 10% sodium hydroxide; the *β*-naphthylhydrazone, m. p. 184—186° (decomp.), and phenylbenzylhydrazone, m. p. 125—126°, are insoluble in warm 10% sodium hydroxide; the *oxime*, m. p. 189—190° (decomp.), yields with sodium hydroxide a green, slightly soluble salt; the *semicarbazone* and *azine* decompose at a high temperature; the former dissolves readily in dilute alkali hydroxide, whilst the latter is insoluble in boiling 10% sodium hydroxide.

The following compounds of 4-nitro-1-hydroxy-*β*-naphthyl methyl ketone are described. The phenylhydrazone, m. p. 222—223° (decomp.), imparts a red colour to cold 10% sodium hydroxide, and gradually dissolves on heating; it is insoluble in a 30% solution, however, and is decomposed when boiled with this reagent. The *a*-naphthylhydrazone decomposes at a high temperature, is insoluble in cold aqueous sodium hydroxide, but on warming renders the solution yellow. The *β*-naphthylhydrazone decomposes at 240°; it is insoluble in cold sodium hydroxide, but decomposes when heated with the solution. 4-Nitro-1-acetoxy-*β*-naphthyl methyl ketone phenylhydrazone acetate,

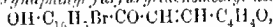


has m. p. 197—198°.

*β*-Hydroxynaphthaldehydephenylhydrazone is insoluble in cold aqueous sodium hydroxide, and decomposes slightly when the solution is heated. The *p*-bromophenylhydrazone, m. p. 194—195° (decomp.), the phenylbenzylhydrazone, m. p. 152—153°, and the benzidine compound,  $\text{C}_{18}\text{H}_{18}(\text{N}\cdot\text{CH}\cdot\text{C}_{10}\text{H}_6\text{OH})_2$ , are insoluble in boiling 10% sodium hydroxide. The *semicarbazone*, m. p. above 240° (decomp.), is readily soluble in cold 10% sodium hydroxide. The phenylhydrazone of the acetyl derivative,  $\text{OAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{HPh}$ , m. p. 164—165°, slowly decomposes when heated with sodium hydroxide solution. The *azine acetate*,  $\text{OAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}\cdot\text{N}_2\cdot\text{CH}\cdot\text{C}_{10}\text{H}_6\text{OH}$ , has m. p. 183—185°. *β*-Hydroxynaphthaldehyde yields two oximes, one of m. p. 148—150° (Horiacher, *Diss.*, 1899), and the other, m. p. 158—160°.

Bromo-1-hydroxy-*β*-naphthyl dibromophenylethyl ketone (benzylidene-2-acetyl-1-naphthol tribromide),  $\text{OH}\cdot\text{C}_{10}\text{H}_6\text{Br}\cdot\text{CO}\cdot\text{CH}(\text{Br})\cdot\text{CHPhBr}$ , m. p. 199°, is slightly soluble in boiling 10% sodium hydroxide, but insoluble in a boiling 30% solution.

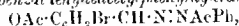
4-Bromo-1-hydroxynaphthyl furfurylideneethyl ketone,



m. p. 154—155°, and the corresponding piperonylidene compound, decomposing at 209—214°, are insoluble in boiling 30% sodium hydroxide. The *p*-nitrobenzylidene compound, m. p. 194—195°, is slightly soluble in 10% sodium hydroxide, but insoluble in a 30% solution.

*o*-Hydroxyacetophenonephenylhydrazone is readily soluble in dilute sodium hydroxide. *o*-Acetoxybenzaldehydephenylbenzylhydrazone has m. p. 137—139°. Benzidine bis-salicylaldehyde is insoluble in cold 10% sodium hydroxide, whilst the corresponding *azine* is readily soluble.

5-Bromo-2-acetoxybenzaldehydeacetylphenylhydrazone,



has m. p. 135—136°. 5-Bromosalicylaldehydeazine, m. p. 305—307° (decomp.), is readily soluble in cold 10% sodium hydroxide. E. G.

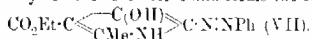
The Optically Active Semicarbazone and Benzoylphenylhydrazone of *cyclohexanone-4-carboxylic Acid*. WILLIAM H. MILLS and (Miss) ALICE M. BAIN (*Proc. Camb. Phil. Soc.*, 1913, 17, 203).—The *semicarbazone* of *cyclohexanone-4-carboxylic acid* can be obtained in an optically active form by crystallising its *morphine* salt from dilute alcohol, the highest value obtained for the molecular rotation in alkaline solution being  $[\alpha]_D + 38.8^\circ$ . The *benzoylphenylhydrazone* of the acid can similarly be obtained in an optically active form by crystallisation of its *quinine* salt from aqueous alcohol, the highest value found for the molecular rotation in alkaline solution being  $[\alpha]_D + 238.6^\circ$ .

These optically active compounds agree so closely in their behaviour with the optically active oxime of this acid previously described by the authors (*l.*, 1910, 97, 1866) that there can be little doubt that the optical activity is due to similar causes in the three cases. The observations, accordingly, lend great support to the view that stereoisomerism in the sense of the Hantzsch-Werner hypothesis exists in the case of semicarbazones and phenylhydrazones. H. W.

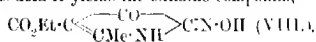
Synthesis of Hydroxypyrrole and Pyrroline Derivatives from Ethyl Aminocrotonate. FRUCH BENARY and BOLESŁAW SILBERMANN (*Ber.*, 1913, 46, 1363—1375).—As might be expected, ethyl  $\beta$ -amino- $\alpha$ -chloroacetylacetonate (A., 1909, i, 888) readily yields pyrrole derivatives when deprived of the elements of hydrogen chloride. The product  $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CH} = \text{C} \cdot \text{OH} \end{smallmatrix}$  (I.) gives a coloration with ferric chloride which is considered to be characteristic of a hydroxypyrrole, but in some cases it reacts in the tautomeric ketonic form  $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CH}_2 - \text{CO} \end{smallmatrix}$  (II.), and yields, *e.g.*, a dipyrroline derivative,  $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{CO} \\ \text{CMe} \cdot \text{NH} \end{smallmatrix} > \text{C} \cdot \text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \cdot \text{CMe} \end{smallmatrix} > \text{C} \cdot \text{CO}_2\text{Et}$  (III.), on oxidation and an indoxylpyrroline,  $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{CO} \\ \text{CMe} \cdot \text{NH} \end{smallmatrix} > \text{C} \cdot \text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > \text{C}_6\text{H}_4$  (IV.), on condensation with isatin.

The ester (I.) could not be hydrolysed, but it condenses in cold concentrated hydrochloric acid to form two bi-molecular compounds which can be easily transformed into one another, and to which the formulae  $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{C(OH)} \\ \text{CMe} \cdot \text{NH} \end{smallmatrix} > \text{C} \cdot \text{C} \begin{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CH} \cdot \text{NH} \end{smallmatrix} > \text{CMe}$  (V.) and  $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{C(OH)} \\ \text{CMe} \cdot \text{NH} \end{smallmatrix} > \text{C} \cdot \text{C} \begin{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CH}_2 \cdot \text{NH} \end{smallmatrix} > \text{CMe}$  (VI.) are assigned.

Like other pyrrole derivatives with a free  $\alpha$ -position, the ester couples with phenyldiazonium chloride and forms the compound

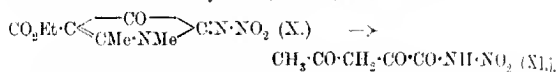


With nitrous acid it yields the oximino-compound,



which exists in two forms, but with sodium nitrite and glacial acetic acid it gives a nitroimine,  $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{CO} \\ \text{CMe}\cdot\text{NH} \end{smallmatrix}\text{>C:N}\cdot\text{NO}_2$  (IX.) (compare Scholl, A., 1905, i, 181; 1906, i, 767), which behaves in water as a nitroimine acid, analogous to nitroic acid (Hantzsch and Kiesel, A., 1900, i, 89). The acidity is not due to the hydrogen atom of the imino group, since this may be replaced by methyl without affecting that property.

The methylated nitroimine (X.) is slowly hydrolysed by cold alkali, when the nitroamide of acetoneoxalic acid (XI.) is formed with elimination of methylamine, alcohol, and carbon dioxide:



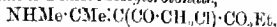
*Ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate* (I.) is prepared by the addition of ethyl  $\beta$ -amino- $\alpha$ -chloroacetylacetonate to alcoholic potassium hydroxide. It forms faintly yellow leaflets which decompose at  $215^\circ$ , reduces ammoniacal silver oxide, gives the pyrrole reaction, and produces a brown coloration in alcohol or a red precipitate in water with ferric chloride. It gives a dark red solution in cold concentrated hydrochloric acid which becomes green in time, and contains a mixture which on fractionation from alcohol deposits the *hydrate of ethyl 3-keto-5:5'-dimethyl-2:3'-dipyrroline-1:4'-dicarboxylate* (VI.) in reddish-brown needles, which are purified by conversion into the unstable, greenish additive compound with hydrochloric acid and leaving in vacuum. It gives no coloration with ferric chloride, and decomposes at  $180^\circ$ . The alcohol mother liquors contain *ethyl 3-hydroxy-5:5'-dimethyl-2:3'-dipyrrole-4:4'-dicarboxylate* (I.), which is precipitated by water, or obtained from the foregoing compound by the action of water, in the form of almost colourless leaflets which decompose at  $157.5^\circ$ , and give the above compound with hydrochloric acid and a transient green colour with ferric chloride.

The indigoid *ethyl bis-2-methylpyrrolino-3-carboxylate* (III.) is obtained in brick-red, microscopic needles, decomp.  $220-225^\circ$ , which give a dark red potassium salt with alcoholic potassium hydroxide. The leuco-compound is grey, but is rapidly oxidised in the air. The *ethyl 2-indolylpyrrolinocarboxylate* (IV.) is a dark red powder, decomp.  $220-225^\circ$ . *Ethyl 5-benzeneazo-4-hydroxy-2-methylpyrrole-3-carboxylate* (VII.) forms brownish-yellow needles, decomp.  $225-226^\circ$ , which give a red colour with ferric chloride in alcohol.

On treating the ester (I.) with sodium nitrite and dilute hydrochloric acid, the  $\alpha$ -form of *ethyl 5-oximino-4-keto-2-methylpyrrolino-3-carboxylate* (VIII.) is obtained. It is purified by means of its potassium salt, and then forms light yellow needles, decomp.  $175^\circ$ . When a few drops of hydrochloric acid are added to the warm alcoholic solution, the  $\beta$ -form crystallises in olive-green leaflets. *Ethyl 5-nitroimino-4-keto-2-methylpyrrolino-3-carboxylate* (IX.) forms shining yellow, flat needles with  $\text{H}_2\text{O}$ , which dissolve in dilute alkalis, give precipitates with silver and lead salts, and respond to the Liebermann and Thiele-Lachman reactions. Both the hydrate

and the anhydrous compound give a brown *additive* compound,  $C_9H_7O_3N_3.NH_3$ , with ammonia.

*Ethyl β-methylamino-α-chloroacetylacetonate*,



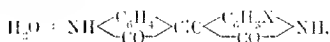
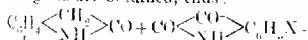
from ethyl methylaminocrotonate and chloroacetyl chloride in presence of pyridine in ether, forms long, white needles, m. p. 50.5–51°. With alkali it yields *ethyl 4-hydroxy-1:2-dimethylpyrrole-3-carboxylate* as a very hygroscopic mass, which, with nitrous acid, gives the analogous *isonitroso*-compound,  $C_9H_{12}O_4N_2$ , in lemon-yellow needles, decomp. 162.5°, which are hydrolysed by cold sodium hydroxide to the *acid*,  $C_8H_8O_4N_2$ , colourless needles, decomp. 154–155°. The *nitroamino*-compound (X) is formed by the action of sodium nitrite and glacial acetic acid in orange needles with  $1H_2O$ , decomp. 200°, which give a brown *additive* compound with ammonia, and dissolve in sodium carbonate solution. The addition of dilute hydrochloric acid after eighteen hours to the red solution in sodium hydroxide precipitates *acetylpyruvonoitroamide* (XI.) in colourless needles, decomp. 258°, which reduce ammoniacal silver oxide, and give a red coloration with ferric chloride. With phenylhydrazine it forms an indole compound,  $C_{17}H_{15}O_3N_3$ , in brick-red, soft needles, decomp. 244°, ammonia being eliminated. J. C. W.

**Syntheses in the Group of the Indogenides.** ANDRÉ WAHL and P. BAGARD (*Compt. rend.*, 1913, 156, 1382–1385).—Condensation of oxindole with cyclic aldehydes and isatin or its chloride in acetic acid solution yields, respectively, *isoindogenides*, *isoindigotin*, and *indirubin* (compare A., 1909, i, 330, 735). This reaction has now been extended, firstly by modifying the conditions of the reaction, and secondly by using substituted i-satins.

Oxindole and isatins condense in alcoholic solution under the influence of sodium ethoxide, giving colourless products, constitutions of which have not yet been determined.

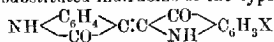
In concentrated sulphuric acid the condensation is accompanied by sulphonation, yielding *isoindigotindi-sulphonic acid*, which is isolated in the form of its *sodium salt*,  $C_{16}H_8N_2O_5(SO_3Na)_2 \cdot 2H_2O$ , crystallising in brown leaflets, which become anhydrous at 100°. It is an acid colour, dyeing wool reddish-orange. Other salts have been prepared, namely: the *calcium salt*, red needles, crystallising with  $5H_2O$ ; the *barium salt*, an amorphous, red powder; the *silver salt*, red needles, crystallising with  $2H_2O$ ; the *nickel salt*, reddish-brown crystals, containing  $5H_2O$ . By decomposing the barium salt with the calculated quantity of sulphuric acid, the free acid, "*isoindigo-carminic*" is obtained, which is very soluble in alcohol and water, and yields an equally soluble *ammonium salt* on the addition of ammonia.

If oxindole is condensed with substituted derivatives of isatin in acetic acid solution, unsymmetrically substituted derivatives of *isoindigotin* are obtained, thus:



By this means *bromoindigotin*, *dibromoindigotin*, *methylo-indigotin*, and *nitroindigotin*, all crystalline compounds, have been prepared.

By the interaction of substituted isatin chlorides and oxindole in benzene solution, substituted indirubins of the type

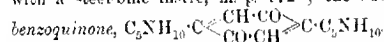


are obtained, isomeric with those prepared by Baeyer's condensation with indoxyl and isatins (compare A., 1911, i, 164, 577). These new indirubins, thus obtained, have a violet colour and dissolve in sodium hyposulphite, giving yellow dye liquors. The mono-substituted derivatives are only slightly fixed on the fibre. Nitroindirubin dyes a violet-black, due to the reduction of the nitro-group by the hyposulphite.

W. G.

**The Condensation of *para*Quinones with Reduced Heterocyclic Nitrogen Compounds.** JULIUS SCHMIDT and AUGUST SIGWART (*Ber.*, 1913, 46, 1491—1497. Compare Möhlau and Redlich, A., 1912, i, 129).—The observation that hexahydrocarbazole when mixed with *p*-benzoquinone in alcoholic solution yields a violet-red liquid from which brown crystals, m. p. 199—200°, soon separate (A., 1912, i, 616) has now been followed up. The product has the composition  $\text{C}_6\text{H}_2\text{O}_2(\text{C}_{12}\text{H}_{11}\text{N})_2$ , that is, bis-hexahydrocarbazyl-*p*-benzoquinone, analogous to the diamino-*p*-benzoquinones (Zucke, A., 1883, 1117) and to diethyldiamino-*p*-benzoquinone (Fischer and Schrader, A., 1910, i, 270). Carbazole and dihydro- and tetrahydro-carbazole do not form such compounds, probably on account of their feeble basic character.

Piperidine and *p*-benzoquinone mixed in cold alcoholic solution gives brownish-violet coloration, followed by a deposit of brownish-violet needles with a steel-blue lustre, m. p. 172°; the substance is *dipiperidyl p*-

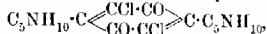


The condensation product of *p*-benzoquinone with tetrahydroquinoline has already been described (Möhlau and Redlich, *loc. cit.*); 1-methyltetrahydroquinoline and 9-methylhexahydrocarbazole gave no condensation products, the crystalline deposit obtained in each case consisting of quinol. Pyrrole reacted with *p*-benzoquinone in alcoholic solution, but the dark crystalline powder, m. p. above 360°, was abnormal in composition, equimolecular quantities of the two substances apparently having entered into reaction. Conine gave a deep coloration, but no solid product. Pyridine, quinoline, and isoquinoline caused only depositions of a nitrogen-free solid, which probably is some polymerisation product of quinone or quinhydrone.

Toluquinone gives rise to condensation products of small crystallising power, for although the expected colorations were obtained with piperidine and hexahydrocarbazole, no crystalline deposits could be obtained; tetrahydroquinoline gives a crystalline compound with toluquinone, but this has already been described (Möhlau and Redlich, *loc. cit.*). Naphthaquinone with hexahydrocarbazole, piperidine, and

tetrahydroquinoline gave deep red alcoholic solutions, but the deposit in each case consisted merely of naphthaquinhydrone.

Tetrachloro-*p*-benzoquinone (chloranil) behaves like *p*-benzoquinone with piperidine, producing *dipiperidyltetrachloro-p benzoquinone*,

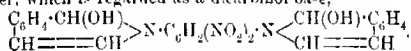


lustrous, bluish-black needles, m. p. 143–144°.

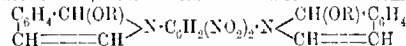
D. F. T.

Action of *iso*Quinoline on 1:3-Dichloro-4:6-dinitrobenzene. THEODOR ZINCKE and G. WEISSFENNING (*Annalen*, 1913, 397, 255–273).—*iso*Quinoline and 1:3-dichloro-4:6-dinitrobenzene react in warm ether to form, after fourteen to fifteen days, *dinitrophenyldiisiquinolinium dichloride*,  $\text{C}_9\text{H}_7\text{N} \cdot \text{C} \begin{array}{c} \text{Cl} \cdot \text{NO}_2 \\ \text{CH} \cdot \text{C}(\text{C}_6\text{H}_3\text{NCl}) \end{array} \text{C} \cdot \text{NO}_2$ , and an orange-red, crystalline  $\psi$ -base,  $\text{C}_{15}\text{H}_{10}\text{O}_5\text{N}_3\text{Cl}$ , m. p. 168° (decomp.), blackening at about 100°.

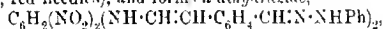
In its behaviour, *dinitrophenyldiisiquinolinium dichloride* resembles partly *dinitrophenyldipyridinium dichloride* (A., 1910, i. 585), partly 2-*op*-*dinitrophenylisiquinolinium chloride* (this vol., i. 389). From it an orange-yellow *dichromate*, yellow *picrate*, m. p. 225°, and *platinichloride*, m. p. 250°, can be prepared. By treating its aqueous solution with sodium carbonate or ammonia, a  $\psi$ -base is obtained, a brownish-red powder, which is regarded as a dicarbinol base,



This  $\psi$ -base regenerates salts of *dinitrophenyldiisiquinolinium* by treatment with acids, is converted into the yellow *betaine* (see below) by boiling dilute acetic acid, reacts with warm alcohols to form *carbinyl ethers*,

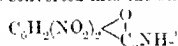


(*methyl ether*, decomp. 180–190°, long, red needles; *ethyl ether*, m. p. 175°, red needles), and forms a *dihydrazide*,



almost black crystals, by warming with alcoholic phenylhydrazine. In methyl alcoholic solution the  $\psi$ -base is converted by nitric acid, D 1.4, into the very characteristic *dinitrophenyldiisiquinolinium dinitrate*,  $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{C}_6\text{H}_3\text{N} \cdot \text{NO}_2)_2 \cdot \text{H}_2\text{O}$ , decomp. 140–150°, colourless needles.

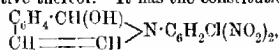
By long keeping with 10% sodium nitrite, *dinitrophenyldiisiquinolinium dichloride* is converted into the *betaine*,



yellow needles. The constitution of the latter, which is also obtained by treating the  $\psi$ -base with boiling 25–30% acetic acid, is proved by the formation of the substance from isiquinoline and 3-chloro-4:6-dinitrophenol at 100°. The *betaine* forms salts (*chloride*, colourless needles, *platinichloride*, *nitrates*) which are hydrolysed by an excess of water. A corresponding *thiobetaine*,  $\text{C}_6\text{H}_2(\text{NO}_2)_2 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{N} \end{array}$ , dark

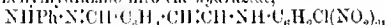
crimson powder, is obtained by treating alcoholic dinitrophenylisoquinolinium dinitrate with hydrogen sulphide; it forms a very unstable *chloride* and *platinichloride*.

The  $\psi$ -base,  $C_{15}H_{10}O_5N_3Cl$ , behaves similarly to the  $\psi$ -base obtained from 2-*op*-dinitrophenylisoquinolinium chloride (*loc. cit.*), and proves to be a chloro-derivative thereof. It has the constitution



forms a *chloride*,  $\begin{array}{c} C_6H_4 \cdot CH \\ | \\ CH=CH \end{array} \gg NCl \cdot C_6H_4Cl(NO_2)_2$ , colourless needles, *platinichloride*, and *nitrate*, and yields ethers by treatment with alcohols in chloroform; the *methyl ether*, m. p. 164–165° (decomp.), dark red needles, and *ethyl ether*, m. p. 156–157°, red leaflets, are described. By boiling with alcohol and aniline, the  $\psi$ -base is converted into 2-phenylisoquinolinium chloride and 3-chloro-4:6-dinitroaniline, the latter being changed to 2:4-dinitro-5-aminodiphenylamine by the excess of aniline.

By warming with water, the  $\psi$ -base is transformed into an *isomeride*,  $C_{15}H_{10}O_5N_3Cl$ , m. p. 168° (decomp.), dark violet-red leaflets, which forms salts with acids very slowly, and does not yield ethers or a hydrazide. On the contrary the  $\psi$ -base is converted by boiling alcoholic phenylhydrazine into the *hydrazide*,



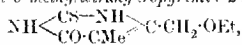
m. p. 155° (decomp.), blackish needles.

C. S.

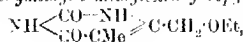
**Preparation of 5:5-Dialkylbarbituric Acids Containing an Unsaturated Hydrocarbon Residue Attached to Nitrogen.** EMANUEL MERCK (D.R.P. 258958. Compare A., 1899, i, 16; 1904, i, 380).—5:5-Diethyl-1-allylbarbituric acid, m. p. 77°, is obtained by heating monoallylcarbamide (20 parts) with diethylmalonyl chloride (40 parts) during fifty hours at 100–120°, whilst the latter compound with diallylcarbamide (sinapoline) furnishes 5:5-diethyl-1:3-diallylbarbituric acid, b. p. 153–157°/9 mm. F. M. G. M.

**Pyrimidines. LXII. Syntheses of Pyrimidines Related Structurally to Pyrimidine-Nucleosides.** THOMAS B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1913, 35, 585–597; *J. Biol. Chem.*, 1913, 14, 307–320).—This work was undertaken with the object of establishing the constitution of the nucleosides. The simplest nucleoside of thymine, namely, 4-hydroxymethyl-5-methyl-tetrahydropyrimid-2:6-dione, has been synthesised in the following manner.

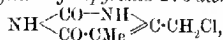
When thiocarbamide is condensed with ethyl  $\gamma$ -ethoxy- $\alpha$ -methylacetoacetate (Johnson, this vol., i, 588) in presence of sodium ethoxide, 2-thio-4-ethoxymethyl-5-methyltetrahydropyrimid-2:6-dione,



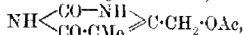
m. p. 191–192°, is obtained, which crystallises in hexagonal tablets. On boiling this substance with chloroacetic acid and water, it is converted into 4-ethoxymethyl-5-methyltetrahydropyrimid-2:6-dione,



m. p. 220°, which forms arborescent crystals, and when heated with concentrated hydrochloric acid at 125–150° in a sealed tube yields 4-chloromethyl-5-methyltetrahydropyrimid-2:6-dione,



m. p. 243°, which crystallises in plates. By the action of silver acetate on this chloro-compound, the acetyl derivative,



m. p. 260–261° (decomp.), is produced, which is hydrolysed by barium hydroxide with formation of 4-hydroxymethyl-5-methyltetrahydropyrimid-2:6-dione,  $\text{NH} \begin{array}{c} \diagup \text{CO-NH} \\ \diagdown \text{CO-CMe} \end{array} \gg \text{C-CH}_2\text{-OH}$ , m. p. 224–225°

(decomp.), which crystallises in needles. An attempt to convert this simple nucleoside into thymine and formaldehyde by hydrolysis with 10% sulphuric acid was not successful, but on heating it with hydriodic acid and amorphous phosphorus it was converted into 4:5-dimethyl-tetrahydropyrimid-2:6-dione (4:5-dimethyluracil). E. G.

**Abnormal Solubility of Colloidal Uric Acid.** LEOPOLD LICHTWITZ (*Zeitsch. physiol. Chem.*, 1913, 84, 416–418).—Polemical. Schade and Bodea (this vol., i, 404) have regarded a supersaturated uric acid solution as a colloid gel. Their views are now criticised. The passage from the aggregate of molecules in drops to the amorphous solid phase, and from this to the crystalline form, takes place with very varying velocity, and the amorphous form can remain stable for a considerable time; it is therefore unnecessary to regard it as a colloid. E. F. A.

**Purines. IX. 6:8-Dihydroxy-2-thiopurine and 6-Hydroxy-2:8-dithiopurine.** The Desulphurisation of Thiopurines. A New Method of Preparing Xanthine. CARL O. JOHNS and ALBERT G. HOGAN (*J. Biol. Chem.*, 1913, 14, 299–306).—6:8-Dihydroxy-2-thiopurine is easily prepared in quantity by heating a mixture of 4:5-diamino-6-hydroxy-2-thiopyrimidine with carbamide.

6-Hydroxy-2:8-dithiopurine is obtained by heating a mixture of 4:5-diamino-6-hydroxy-2-thiopyrimidine and thiocarbamide.

Hypoxanthine-2-thiolacetic acid and 6:8-dihydroxypurine-2-thiolacetic acid can be boiled with water for hours without undergoing notable decomposition. When boiled with 20% hydrochloric acid they are hydrolysed to xanthine and uric acid respectively. 6-Hydroxypurine-2:8-dithiolacetic acid is more stable, and it is not desulphurised by boiling for several hours with 20% hydrochloric acid, although a small quantity of a dihydroxypurine monothiolacetic acid is obtained.

6:8-Dihydroxy-2-thiopurine,  $\text{NH} \begin{array}{c} \diagup \text{CO-C-NH} \\ \diagdown \text{CS-NH-C-NH} \end{array} \gg \text{CO}$ , forms minute needles, which do not melt at 310°; they give a brilliant murexide reaction. The corresponding 6:8-dihydroxypurine-2-thiolacetic acid has decomp. 225°.

Hypoxanthine-2-thiolacetic acid,  $\text{CO-H-CH}_2\text{-N} \begin{array}{c} \diagup \text{NH-C-C-NH} \\ \diagdown \text{C=N-C-N} \end{array} \gg \text{CH}_3$ ,



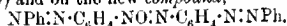
prepared by the action of monochloroacetic acid on thiohypoxanthine, decomposes at  $240^{\circ}$ , forming a violet-coloured substance. It is decomposed quantitatively on boiling with 20% hydrochloric acid into xanthine. This forms the most convenient procedure of preparing puro xanthine in quantity; it is not necessary to isolate the intermediate thiolacetic acid.

E. F. A.

Considerations and Experiments on the Constitution of the Azoxy-compounds. I. and II. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 201—213, 282—293).—A summary and discussion of the work of the author with various collaborators published in recent years.

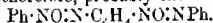
R. V. S.

Polyazoxy-compounds. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 356—360).—The paper deals with the action of hydrogen peroxide in acetic acid solution on bisbenzeneazobenzene (Mills, T., 1895, 67, 929) and on the new compound,



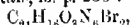
This substance is prepared by the action of sodium ethoxide on *p*-nitroazobenzene; it crystallises in red laminae, m. p. about  $215^{\circ}$ .

Bisbenzeneazobenzene, when treated with hydrogen peroxide and glacial acetic acid, yields *bisbenzeneazoxybenzene*,  $\text{C}_6\text{H}_4(\text{N}_2\text{O}\cdot\text{Ph})_2$ , which forms lustrous, yellow laminae, m. p.  $155^{\circ}$ . It yields a *dibromo*-derivative,  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_4\text{Br}_2$ , which forms yellow crystals, m. p. about  $200^{\circ}$ . The azoxy-compound has, therefore, probably the formula



On treatment with concentrated sulphuric acid for one hour on the water-bath, it yields a product from which a substance,  $\text{C}_{18}\text{H}_{14}\text{O}_4$ , can be extracted with benzene; it forms yellowish-green leadets, m. p.  $185^{\circ}$  (yielding a red liquid), and is probably the *p*-hydroxyazoxy-compound,  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ .

*Azoxybisazoxybenzene*,  $\text{Ph}\cdot\text{N}_2\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{O}\cdot\text{Ph}$ , is obtained from the corresponding triazo-derivative above mentioned; it forms lustrous, golden-yellow crystals, m. p.  $230^{\circ}$ . It yields a *dibromide*,



which is a yellow, microcrystalline powder, decomposing about  $265^{\circ}$ , and in consequence the structural formula of the azoxy-compound is probably  $\text{Ph}\cdot\text{N}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NO:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO:N}\cdot\text{Ph}$ . The triazoxy-compound also suffers Wallach's re-arrangement, for on warming with sulphuric acid an intense blue coloration is obtained.

R. V. S.

The Relation between the Metallic Salts and the Soluble Carbonates and its Bearing on the Precipitation of Proteum. W. NEVILL HEARD (*J. Physiol.*, 1913, 46, 104—129).—Since thorough dialysis removes all precipitation of emulsoid protein by salts of the heavy metals, precipitation must be associated with some removable constituent. The experiment of adding salts to such dialysed solutions shows that the production of a substance with a very low solubility product is the necessary condition in causing precipitation. The only salt in the dialysate which is capable of producing this result is a hydrogen carbonate, except in the case of silver. The reaction of these metals with emulsoid protein closely follows the reaction of these

metals with soluble hydrogen carbonates, and the conclusion is therefore drawn that the process depends on this reaction. Probably the precipitation with hydrogen carbonates and carbonates acts mainly by the removal of the hydroxyl ions freed by the hydrolysis of these salts. But the results with silver nitrate and sodium chloride suggest that there are other factors.

W. D. H.

**The Soluble Metallic Compounds of Sulphurised Proteins, with Special Reference to Copper.** ROBERT UHL (*Zeitsch. physiol. Chem.*, 1913, 84, 478—496).—The preparation is described of sulphur-protein compounds from various proteins by means of carbon disulphide. It is analogous to the preparation of dithiocarbamates from aliphatic amines. These substances are converted by salts of the heavy metals in presence of alkali into metal-sulphur-protein compounds which are soluble in water, and in which the sulphur is united to the metal. The compounds with copper, silver, and mercury have a high content of metal, are resistant to alkali, are not precipitated by protein solutions, are resistant to proteolytic enzymes, and do not diffuse through an animal membrane. Sulphur-peptone given subcutaneously or intravenously is relatively non-toxic. Its copper compound is also relatively non-poisonous, and produces no local reaction; the animal resists doses of copper five times greater than when given in any other way. It is deposited in most of the organs except the brain and heart; most appears in the liver, and is then secreted into the bile. It has but little effect on blood pressure, and inhibits diuresis. It is bactericidal to staphylococci, but has no action on anthrax or trypanosomes.

W. D. H.

**Method of Preparing Ash-free Caseinogen and Casein** LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 203—206).—The ash-free proteins were prepared by alternate precipitation with dilute acid and solution in dilute ammonia several times, the last portion of calcium being removed by ammonium oxalate; after this the protein is precipitated with dilute acid and purified by treatment with water, alcohol and ether, being finally dried over sulphuric acid under reduced pressure. Elementary analyses are given of both proteins; the figures are very similar.

W. D. H.

**Preparation and Composition of Basic Calcium Caseinogenate and Caseinate.** LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 207—209).—Basic calcium caseinogenate and caseinate were prepared by treating the ash-free protein with calcium carbonate, or by dissolving the protein in lime-water and neutralising with hydrochloric acid. In the first reaction, the amount of carbon dioxide displaced by the protein was estimated, and also the amount of calcium in the resulting product. In the second method the calcium was also estimated. The compound contains 1.78% of calcium.

W. D. H.

**Preparation and Composition of Unsaturated or Acid Caseinogenates and Caseinates.** LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 211—225).—These were prepared

by dissolving the ash-free protein in  $N/50$ -sodium, potassium or ammonium hydroxide, and careful neutralisation with hydrochloric acid. The caseinates contain twice the amount of the basic element present in the caseinogenates. Such compounds are monobasic. With calcium, strontium, and barium, monobasic and dibasic compounds were obtained; in the caseinates twice the amount of base combines with the protein molecule as combines in the caseinogenates. W. D. H.

**Valency of Molecules, and Molecular Weights of Caseinogen and Casein.** LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 227—230).—From the study of the caseinogenates and caseinates, the molecular weight of caseinogen is given as 8888, and of casein as 4444. The valency of the protein molecule in basic caseinogenates is 8, in basic caseinates, 4. W. D. H.

**Composition and Properties of the Brine-soluble Compound in Cheese.** LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 231—236).—The protein in cheese which dissolves in warm 5% solution of sodium chloride is mono-calcium caseinate, formed from calcium caseinate by removal of part of its calcium by lactic acid produced from lactose in the process of cheese-making. W. D. H.

**Formation of Porphyrin. II. Porphyrinogen and its Relation to the Blood-Pigment and its Derivatives.** HAAS FISCHER, ERICH BARTHOLOMÄUS, and HEINRICH ROSE (*Zeitsch. physiol. Chem.*, 1913, 84, 262—287. Compare this vol., i, 409).—Porphyrinogen, the first crystalline, colourless reduction product of the blood pigment, is obtained by the action at the ordinary temperature of glacial acetic acid and hydrogen iodide, in presence of phosphonium iodide, on hæmin, mesoporphyrin or hematoporphyrin. It is also obtained from the last two substances by reducing in alkaline solution with sodium amalgam, or with zinc dust and iron. Porphyrinogen is readily reconverted into mesoporphyrin by means of sodium methoxide, methyl alcoholic potassium hydroxide, alkaline potassium ferrioxalate, or by exposure to atmospheric oxidation in neutral or alkaline solution.

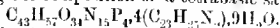
Sodium methoxide splits off phyllopyrrole from porphyrinogen. The complete reduction is similar to that of hæmin. On oxidation, methyl ethylmaleimide and hæmatic acid are obtained. When administered to animals, porphyrinogen has a sensibilising action, whereas mesoporphyrin has no action.

Use is made of the sparingly soluble sodium salt for the purification of mesoporphyrin. On total reduction of mesoporphyrin, phyllopyrrole is obtained with other products. E. F. A.

**Behaviour of the True Nucleic Acids to Dyes. II.** R. FERTIG (*Zeitsch. physiol. Chem.*, 1913, 84, 309—328. Compare A., 1912, i, 926).—Nucleic acid gives precipitates with basic dyes, but none with acid dyes. It is necessary to add the solution of sodium nucleate to the dye, otherwise the formation of colloidal gels prevents precipitation.

Nucleic acid and tetramethyldiaminotriphenylcarbinol give a

precipitate having the composition of a tetrabasic salt,



Treatment with alcohol extracts the dye, leaving a more or less colourless residue. It is considered that an ethyl ether of the dye and nucleic acid are formed.

The compound with hexamethyl-*p*-rosaniline is also tetrabasic, namely,  $\text{C}_{42}\text{H}_{57}\text{O}_{24}\text{N}_{15}\text{P}_4\cdot 4(\text{C}_{25}\text{H}_{39}\text{N}_3)_2\cdot 9\text{H}_2\text{O}$ . It forms a remarkable jelly during the preparation, which can be drawn out into very long threads. It is remarkable in being entirely soluble in methyl alcohol. Some decomposition takes place in alcoholic solution, part of the dye being eliminated.

The substances are considered to be chemical rather than adsorption compounds, and the whole of the phosphorus is shown to be fixed as nucleic acid.

Crystal-violet is a very suitable precipitant for nucleic acid, and may be used to purify it.

Methylene-blue gives a precipitate with nucleic acid, which is readily filtered and washed. It is entirely indifferent towards all solvents, and in no case could the dye be eliminated.

E. F. A.

**Preparation of an Iron Derivative of Iodoparanucleic Acid.** KSOLL & Co. (D.R.-P. 258297. Compare A., 1909, i, 275).—

When the iron derivative of paranucleic acid (Salkowski, A., 1901, i, 242, 434) is dissolved in 8% hydrochloric acid, and treated at 50° with a solution of iodine in potassium iodide, it furnishes the *iron* derivative of *iodoparanucleic acid*, a reddish-brown powder which has therapeutic properties and contains: iodine = 8%, iron = 13%, phosphorus = 2%, and nitrogen = 12%.

It can also be prepared from iodocaseinogen, pepsin, and a solution of iron alum; or by the action of iodine on paranuclein in the presence of iron alum.

F. M. G. M.

**Action of Quinones on Wool and Other Protein Substances.** WASSILI W. SCHARVIN (*Zeitsch. angew. Chem.*, 1913, 26, 254).—Wool is dyed reddish-brown when acted on by the vapour or solutions of *p*-benzoquinone. Derivatives of *p*-benzoquinone act in a similar manner, the rate of reaction and colour depending on the compound employed; anthraquinone and phenanthraquinone are without action on wool.

Silk, leather, casein, egg-albumin, gelatin, etc., are dyed similarly by *p*-benzoquinone and its derivatives.

The conclusion is drawn that the quinone reacts with the amino-groups in the protein, and in the case of chloro-derivatives it is found that part of the chlorine is eliminated as hydrogen chloride, although chlorine can also be detected in wool dyed with dichloro-benzoquinones.

W. H. G.

**Preparation of Fibrinogen by Dialysis Against Sucrose Syrup.** MAURICE PIETRE and ANTOXY VILA (*Compt. rend.*, 1913, 156, 1182–1185). The plasma is demineralised by dialysis against a syrup of sucrose followed by dialysis against distilled water. The

plasma, placed in a collodion bag, is first immersed in the sugar syrup for eight to ten hours, then removed, and the bag and contents placed in distilled water until the contents of the bag have returned to their original volume. By this means practically the whole of the mineral substances are removed, and the fibrinogen is deposited during the second operation, thus being isolated in the minimum of time with the use of but little liquid.

W. G.

**$\beta$ -Glutokyrine Sulphate.** MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1913, 84, 288-299).—By the action of silver salts and barium hydroxide on glutokyrine a simplification of the glutokyrine molecule is brought about (compare Levene and Birchard, this vol., i, 109). There is no evidence that the silver and barium hydroxide treatment leads to a separation of the constituents of a mixture of kynes. The quotient  $\text{CO}_2/\text{N}$  becomes smaller after treatment, but there is no increase in the nitrogen measured by Sørensen's formaldehyde method, indicating that no peptide linkings have been destroyed. On hydrolysis of the various fractions obtained during the treatment, arginine and lysine were obtained.

E. F. A.

**The Rate of Destruction of Pepsin by the Direct Electric Current.** W. E. BURGER (*Amer. J. Physiol.*, 1913, 32, 41-43).—The digestive activity of a solution of pepsin is decreased (as is that of ptyalin) by the passage through it of a direct electric current at a uniform rate per unit of current.

W. D. H.

**A New Method of Isolating Trypsin.** HENRY LEONOR HOLZBERG (*J. Biol. Chem.*, 1913, 14, 335-339).—The addition of safranin to aqueous solutions of Grubler's or Fairchild's trypsin, or to aqueous extracts of the pancreas causes a precipitate which is strongly proteolytic. The precipitate contains safranin, and is sparingly soluble in water. Removal of the safranin, or an increase in water solubility has not yet been accomplished. The precipitates produced by alcohol, or by a mixture of alcohol and ether in the mother liquor are practically devoid of proteolytic activity.

W. D. H.

**The Enzymes of the Pancreas. II. The Action of Calcium Salts in the Generation of Trypsin from Trypsinogen.** JOHN MELLANDY and V. J. WOOLLEY (*J. Physiol.*, 1913, 46, 159-172).—Salts of barium and strontium activate pancreatic juice as effectively as salts of calcium. On the addition of these salts to the juice the carbonate is precipitated, and the inhibiting alkali (sodium carbonate) is thus removed; the enterokinase (which is always present in the juice, although in variable amounts) is then allowed to act and convert trypsinogen into trypsin.

W. D. H.

**Action of Ammonia on Invertase. IV.** THEODORE PASZIL (*Zeitsch. physiol. Chem.*, 1913, 84, 408-416. Compare this vol. i, 113, 541). Invertase takes up rather more dry ammonia than diastase. Some of the ammonia is not removed in a vacuum, and nitrogen determinations indicate that part has combined with some constituent

of the enzyme. The treatment does not affect the activity of the enzyme, but after the removal of the ammonia in a vacuum the activity is less, indicating that some such chemical process as the formation of an anhydride is concerned. The conclusion is drawn that the presence of free carboxyl groups is necessary for the enzyme activity. The mere addition of ammonia to form ammonium salts and aldehyde additive compounds has no effect on the specific activity. There is thus a difference in the active chemical groups in diastase and invertase as already indicated in the experiments (*loc. cit.*) with anhydrous hydrogen chloride. E. F. A.

**Synthetical Properties of Emulsin.** VERNON K. KRIEDEL (*Biochem. Bull.*, 1913, 2, 227).—An emulsin which produced *L*-mandelonitrile from amygdalin, two years later produced the *D*-variety. This is explained by the supposition that the fresh emulsin contains two enzymes, one of which synthesises the *D*-nitrile from benzaldehyde and hydrocyanic acid, whilst the other, which is less stable, synthesises the *L*-nitrile. Fresh emulsin from sweet almonds produces the *L*-, and from bitter almonds the *D*-nitrile. W. D. H.

**The Biochemical Synthesis of  $\beta$ -Methylglucoside in a Neutral Liquid, not Participating in the Reaction.** EMILE BOURQUELOT and EM. VERDON (*Compt. rend.*, 1913, 156, 1264—1266; *J. Pharm. Chim.*, 1913, [vii], 7, 482—486).—Emulsin, although insoluble in acetone, will bring about the synthesis of  $\beta$ -methylglucoside by its action on a solution of dextrose and methyl alcohol in acetone containing 20% of water. This synthesis in acetone solution is as complete as in alcoholic solution, but is somewhat slower at first. Thus the ferment is capable of synthesising and hydrolysing glucosides in a neutral liquid, such as acetone, in which it is completely insoluble (compare A., 1912 i, 593). W. G.

**The Enzymes of the Character of Emulsin.** LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1913, 50, 486—496).—Adopting Euler's suggestion as to nomenclature, the enzyme which brings about the hydroxynitrile synthesis is termed the *oxynitrilase*, whereas that which causes the scission of the former substance is called the *oxynitrilase*. The conclusion is drawn that oxynitrilase is not identical with  $\beta$ -emulsin (amygdalase + prunase), because (1) a preparation which has been heated for some time at 40° can still cause the synthesis of an optically active nitrile, whereas it does not lead to the decomposition of amygdalin. (2) A preparation which has been treated successively with acid and then with alkali (to neutralise the acid) behaves in a similar way. (3) Filtrate from the precipitates produced by copper sulphate, by saturation with magnesium sulphate or half-saturation with ammonium sulphate, produce no synthetic action, although they exert the degrading action. The experiments on which these conclusions are founded did not, however, always yield concordant results. The conclusion is also drawn that oxynitrilase and oxynitrilase are different. The grounds are (1) that the latter is more rapidly inactivated by the action of benzaldehyde cyanohydrin.

- (2) In several fruits of *Umbelliferae*, only the oxynitrilase is present.  
 (3) Preparations can be artificially obtained which contain only the oxynitrilase.

S. E. S.

**Reversible Enzyme Action. Hydrolysis and Synthesis of Fats by a Lipase.** Ugo Lombroso (*Chem. Zentr.*, 1913, i, 1043—1044; from *Arch. Pharmacol. experim.*, 1912, 14, 429—459).—Pancreatic secretion and intestinal juice were used as sources of lipase. At 37° hydrolysis of fats sets in immediately and continues until 80% has been changed. Synthesis is slow, requiring thirty to forty hours before it can be detected, and the amount is extremely small. The addition of bile had not the slightest effect on the synthetic process, but it accelerates the hydrolytic changes. Prolonged heating at 49° damages the hydrolytic enzyme, but does not affect the synthetic. Glycerol lessens the destructive influence of heat, but oleic acid has no such influence. The synthetic enzyme in the pancreas is not favoured by prolonged contact with either glycerol or oleic acid before these are mixed. Pancreatic juice preparations which contain the synthetic enzyme have only feeble lipelastase properties. The addition of fats retards the synthetic changes, but does not stop them. Intestinal secretions which are active hydrolytically have no synthetic activity.

E. F. A.

**Enzyme Action. V. Action of Neutral Salts on the Activity of Castor Bean Lipase.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, 35, 601—616. Compare Falk and Nelson, A., 1912, i, 522, 593; Falk and Hamlin, this vol., i, 303; Falk, this vol., i, 433).—An account is given of experiments to determine the influence of neutral salts on the activity of a castor bean lipase preparation towards ethyl butyrate. In all cases, the change in the activity was found to be a continuous function of the concentration of the added salt. The activities, as compared with those of pure aqueous solutions, were decreased by the uni-univalent salts, by the chlorides and nitrates of barium and calcium (except for dilute solutions) and magnesium, by sodium oxalate, and by dilute solutions of sodium sulphate. The activities were increased by dilute solutions of the chlorides of barium and calcium, by concentrated solutions of sodium sulphate, by magnesium sulphate, and by manganous chloride and sulphate. Potassium sulphate solutions did not affect the activity.

The retarding action is probably due to coagulation of the enzyme by the salts, the ions of which produce their individual specific effects in each case. The accelerating action cannot be so easily explained, except perhaps for cases in which an increased formation of active lipase may be assumed (compare Falk and Hamlin, *loc. cit.*). E. C.

**Enzyme Action. VI. Specificity of Lipase Action.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, 35, 616—624).—An account is given of the effect of methyl and ethyl alcohols, acetone, glycerol, and dextrose on the activity of a preparation of lipase from the castor bean. Solutions of the alcohols and acetone exerted an inhibiting action on the hydrolysis of ethyl butyrate, the effect increasing with the con-

centration, but solutions of glycerol and dextrose did not produce any inhibiting effect except perhaps in concentrated solutions. It is considered probable that the simpler esters exert a specific inhibiting action on the activity of lipase similar to that exerted by the simpler alcohols, and that higher esters exert a smaller inhibiting action like that exerted by glycerol. This view is in harmony with the results obtained on testing the activity of castor bean lipase with solutions of methyl and ethyl acetates, ethyl butyrate, and glyceryl triacetate. In the light of these results, glyceryl triacetate is regarded as the most suitable ester for testing lipolytic activity.

E. G.

**Enzyme Action. VII. Further Study of the Hydrolytic Action of Amino-acids on Esters.** MARSTON LOVELL HAMLIN (*J. Amer. Chem. Soc.*, 1913, 35, 624—632).—In continuation of the study of the hydrolytic action of certain amino-acids on esters (Falk and Nelson, A., 1912, i, 593) it has been found that glycine, glutamic acid, and aspartic acid exert a varying action on methyl and ethyl acetates, glyceryl triacetate, phenyl acetate, ethyl butyrate, and ethyl and phenyl benzoates. If these esters are arranged in the order of decreasing amounts of hydrolysis, the order varies with the hydrolytic agent used, namely, water, glycine, or glutamic or aspartic acid, and this indicates that the action is selective. Solutions containing both glycine and acetic acid exert a smaller hydrolytic action on methyl acetate and ethyl butyrate than do solutions of acetic acid alone.

E. G.

**Preparation of Thrombokinase from Fibrin.** H. L. F. BUSWELL (*Proc. Physiol. Soc.*, 1913, iii; *J. Physiol.*, 46).—Distilled water extracts thrombokinase from washed fibrin, but not thrombin.

W. D. H.

**Glyoxylase.** HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, 14, 423—431).—The catalyst, *glyoxylase*, studied converts methylglyoxal into lactic acid, and phenylglyoxal into mandelic acid. Evidence is presented that the agent is an enzyme; it is contained in aqueous extracts of muscle, liver, blood corpuscles, yeast cells, and the tissues of the oyster, but not in serum, potatoes, or cultures of the *B. vulgaricus*. The acids yielded are mixtures of the *levo*- and inactive forms. It is possible that more than one enzyme is concerned.

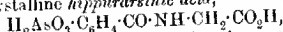
W. D. H.

**Compounds of Carboxyarylarsinic Acids with Amino acids Derived from Proteins. Hippuroarsinic Acid.** LOUIS HEGGONENQ and ALBERT MOREL (*J. Pharm. Chim.*, 1913, [vii], 7, 383—389).—Hippuroarsinic acid and arsenohippuric acid have been prepared, and their physiological actions compared with those of benzoarsinic acid and arsenobenzoic acid.

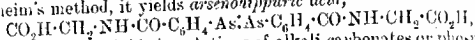
Dichloroarsinobenzoyl chloride (Fourneau and Ochshin, A., 1912, i, 928) reacts with glycine in presence of *N*-sodium hydroxide solution to give a liquid from which, on addition of hydrochloric acid, hippur-



arsine oxide is precipitated along with some benzarsine oxide. This precipitate on solution in sodium hydroxide solution is oxidised by hydrogen peroxide to a mixture of benzarsinic and hippuroarsinic acids, and the former is precipitated completely on adding hydrochloric acid in excess. The filtrate is made alkaline and concentrated under reduced pressure. On adding alcohol there separate *trisodium hippuroarsinate*,  $\text{Na}_3\text{AsO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Na} \cdot 4\text{H}_2\text{O}$ , which crystallises from alcohol in needles, and on treatment with alcohol and hydrochloric acid furnishes crystalline *hippuroarsinic acid*,



which is very soluble in water, but like the analogous substance decomposes when its aqueous solution is boiled with calcium or barium chloride or magnesia mixture. On reduction by Ehrlich and Berthelm's method, it yields *arsenohippuric acid*,



a yellow powder, soluble in solutions of alkali carbonates or phosphates, forming unstable solutions, which deposit highly toxic arsine oxides, but gives solutions in alkali hydroxides, which are stable in the absence of air, and have a toxicity similar to those of solutions of arsenobenzoic acid.

T. A. H.

## Physiological Chemistry.

**Calorimetrical Experiments on Warm-blooded Animals.**  
ARCHIBALD V. HILL and (Miss) A. M. HILL (*J. Physiol.*, 1913, 46, 81—103).—An automatic self-registering respiration calorimeter for small, warm-blooded animals is described; by its use it is possible to estimate within 2% the total heat liberated. In fasting rats at 15°, the heat production per gram is constant if the animals are more than one-third the size of the full-grown animal; for smaller specimens the figure rises rapidly, and may reach 70% greater than for grown animals. If the body surface is  $S$ , and the weight  $W$ , then in rats,  $S \cdot W = 10 \times 10^3$ . The rate of heat production to  $S$  during inanition is not constant, being 140 cal. per sq. cm. for small animals, 99 for medium-sized, and 110 for large animals. Any assumption that heat production is determined by heat loss is therefore unjustifiable. The high value in small animals is probably not due to their smallness, but to their youth, and consequently high chemical activity. Rats fed on biscuit at 15° give out 13% more heat than when fasting. If this is due to Rubner's specific dynamic value of foodstuffs, it suggests that the animals, even when fasting, give out more heat than is necessary to keep them warm. If the animals are kept in the calorimeter in groups, the heat production is lessened, because contact prevents heat loss, and especially as company promotes sleep and rest; they certainly grow faster.

W. D. H.

**Oxygen Capacity of the Blood Pigment.** WILHELM MANCHOT (*Zeitsch. physiol. Chem.*, 1913, 84, 306-308).—Polonina. A reply to Burn (this vol., i, 306) and to Butterfield (A., 1912, ii, 820).  
E. F. A.

**The Phosphorus content of the Blood of Normal and Parathyroidectomised Dogs.** ISIDOR GREENWALD (*J. Biol. Chem.*, 1913, 14, 369-379).—After removal of the parathyroid glands, the total phosphorus of the blood and serum is increased, even at a time when the tremors are slight. The increase may be as much as 160 mg. of phosphorus per kilo. of blood. The greater part of this increase is in the fraction which is insoluble in the usual lipid solvents, but is soluble in a mixture of dilute hydrochloric or acetic and picric acids.  
W. D. H.

**Formation of Lactic Acid from Dextrose, Glyceraldehyde, and Dihydroxyacetone in the Blood of the Ox and Pig.** ADAM LOEB (*Biochem. Zeitsch.*, 1913, 50, 450-456).—The red corpuscles of the ox and pig, which do not cause glycolysis of either the blood-sugar or added sugar, and only produce a small amount of lactic acid, nevertheless show either as high (pig) or even a higher (ox) capacity for producing lactic acid from glyceraldehyde than the blood of the dog, which has considerable glycolytic action. The red corpuscles of the pig have, furthermore, a considerably greater capacity than those of either the dog or ox of converting dihydroxyacetone into lactic acid.  
S. B. S.

**The Formation of Lactic Acid from Carbohydrates in Laked Blood.** WALTER GRIESBACH (*Biochem. Zeitsch.*, 1913, 50, 457-464).—From the blood of the ox and dog, cell-free blood solutions can be obtained, which, while they do not act on dextrose, can convert *D*-glyceraldehyde and dihydroxyacetone into lactic acid as vigorously as the intact corpuscles. A mixture of racemic and *D*-lactids is thereby produced, as is the case when the intact corpuscles are employed. The conclusion is drawn that the degradation of sugar into lactic acid takes place in two phases, and by two ferments; in the one phase the conversion of the dextrose into glyceraldehyde takes place, and this action is only possible when the cells are intact; in the second phase, the aldehyde is converted into lactic acid, and for this process the intact cell is not necessary.  
S. B. S.

**The Estimation of the So-called "Residual Reduction" of the Blood.** PAUL MAYER (*Biochem. Zeitsch.*, 1913, 50, 362-368).—By "residual reduction" is meant the reduction of Fehling's solution after the sugar in the blood has been removed by fermentation with yeast. It is now shown that pure dextrose solutions (0.1%), after treatment with various races of pure yeasts, also show a "residual reduction," after removal of proteins, etc., by colloidal iron hydroxide. This is due to substances derived from the yeast itself, and the concentrated solutions, after treatment, show reactions for amino-acids and, in most cases, also for purine substances.  
S. B. S.

**The Formaldehyde Titration of Proteins. II.** FRIEDRICH OBERMAYER and ROBERT WILLHEIM (*Biochem. Zeitsch.*, 1913, 50, 369—385. Compare A., 1912, ii, 399).—It is possible, by SÖRENSEN'S method, to estimate the reactive amino-groups in a protein, and the ratio of this reactive amino-nitrogen to the total nitrogen is designated the "amino-index." In euglobulin the mean value (21.5) of the index is higher than that of albumin (about 12). In mammals the value for pseudoglobulin is about the same as that for euglobulin, but in birds it does not differ very much from that of albumin (the mean value is about 15). By means of the determination of this index it is possible to show that the various protein fractions of serum are not homogeneous substances. It is also possible to demonstrate differences in the sera of different species, and the fraction salted out by 25—30% ammonium sulphate has a higher "amino-index" in the case of a hen (28.5—32.5) than in the case of an ox (19—21.5). The serum of the horse is similar to that of the ox, and the serum of the goose is similar to that of the hen; it is therefore possible that the "amino-index" of a definite fraction may be characteristic for definite classes of animals.

S. B. S.

**The Specificity of Immunity Reactions, and their Explanation as Colloidal Chemical Phenomena.** KURT LANDSTEINER (*Biochem. Zeitsch.*, 1913, 50, 176—184).—The author does not regard the contention of Michaelis and Davidsohn (this vol., i, 121), that certain immunity reactions are not of colloidal chemical character, as justified. The view was arrived at on the ground that certain precipitin reactions are independent to a large extent of the hydrogen ion concentrations. Attention is especially called to the fact that serum, blood corpuscles, etc., of different species exert a maximum action in the presence of different hydrogen ion concentrations. This point is illustrated by the adsorption of ricin agglutinin, by the different strengths of acid or alkali which hydrolyse the corpuscles, by the differences in the agglutination of streptococci, and the differences in the precipitability of the sera precipitating reagents.

S. B. S.

**The Coagulation of the Blood. The Significance of Various Physico-chemical Processes in the Action of Thrombin.** M. LANDSBERG (*Biochem. Zeitsch.*, 1913, 50, 245—272).—The temperature curve of reaction velocity of blood coagulation is the result of at least two concurrent processes. The main process is the reaction between the thrombin and fibrinogen, and is apparently of a chemical character. The other reaction, which is antagonistic to the first, is an inhibition of the thrombin action due to its adsorption by the proteins of the serum. Both processes are accelerated by increase of temperature, which exerts therefore a twofold influence on the clot formation. The temperature curve depends to a large extent on the conditions of the experiment. In such combinations, in which the adsorption process is reduced to a minimum, the clotting reaction resembles a fermentative process with an optimal temperature of 35—40°. In the combination

magnesium sulphate plasma; Schmidt's thrombin, which is particularly favourable to adsorption processes, there is a diminution of the reaction velocity even at 17--20°. The adsorption of thrombin by the serum proteins increases with temperature, and is only partly reversible. The conversion of the serum thrombin into its inactive "metathrombin" form is simply due to adsorption; the reactivation by Schmidt's method by means of alkalis being simply the breaking down of the adsorption compound. The general results indicate that there are no facts which are antagonistic to the idea of a fermentative process in clotting.

S. B. S.

**Water Drinking. XIV. The Digestive Efficiency of Saliva as Increased by Dilution with Water.** OLAF BERGELM and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1913, **35**, 461--476).—Mattill and Hawk (*A.*, 1912, ii, 65) have shown that the drinking of large volumes of water with meals increases the amount of carbohydrate digested. Experiments which have now been made *in vitro* show that the dilution of normal human saliva increases its digestive efficiency. The optimum dilution depends on the nature of the diluent, and is 4 volumes for 0.3% sodium chloride solution and 7 volumes for water. Water, softened by the addition of lime water, exerts an inhibiting effect, due principally to the presence of magnesium hydroxide.

E. G.

**The Action of Sugar on Digestion.** ERWIN TUOMSEX (*Zeitsch. physiol. Chem.*, 1913, **84**, 425--436).—Sucrose has no direct action on the stomach, or on the secretion of pancreatic juice and bile. Its action on the small intestine is due to prolongation of gastric digestion without altering the secretions. The lengthening of gastric digestion is due to the occurrence of long pauses in the emptying of the stomach. Sucrose is completely or almost completely absorbed in the small intestine in large quantities, but it delays the absorption of the chyme.

W. D. H.

**The Pepsin-Chymosin Question.** A. KAROZY (*Zeitsch. physiol. Chem.*, 1913, **84**, 329--353. Compare *A.*, 1911, i, 827).—The question of the identity of the milk coagulating and protein digesting enzymes is bound up with nature and age of the animal. Hasselt (*A.*, 1911, i, 248), Porter (*A.*, 1911, i, 698), and Burge (*A.*, 1912, i, 118) have all established the presence of a special milk coagulating enzyme in the stomach of the calf. In such instances where the two enzymes are present they can be separated by Hämmersten's casein method, but with the stomach infusions from other animals which contain no chymosin no such separation could be effected. The power of coagulating milk is inseparably bound up with the pepsin enzyme.

In a similar manner elastin may be used to absorb pepsin, whereas it has no effect on chymosin. This method enables the two enzymes to be separated in the gastric juice of the calf, but not in that of other animals. In slightly acid solution (A 200-hydrochloric acid) elastin adsorbs chymosin, but there is no action when the acidity

is increased (N/80 acid). On digestion with water, the adsorbed chymosin is recovered from the edestin.

Pepsin in the ox and in the calf appears to have the same properties, and that derived from the two sources is the same.

Milk is coagulated in the stomach in all mammals from the first day of life onwards. The ruminants and such animals as the horse and the pig secrete both pepsin and chymosin. Human beings secrete pepsin only, whilst in dogs and cats neither pepsin nor chymosin is present, and the coagulation is due to other factors which are at present but imperfectly understood. E. F. A.

**Formation of Plastein.** I. P. GLAGOLEV (*Biochem. Zeitsch.*, 1913, 50, 162—175).—Formation of plastein has characteristics of a fermentative character, in that it takes place in the presence of minute quantities of the digestive fluid, requires a certain definite retention of the medium, and does not take place if the digestive fluid is lost, boiled. It appears to be a generative process, in that when produced by rennin powder (Witte's), natural gastric juice, or papayotin, there is a diminution of the reactive amino-groups, as determined by Sørensen's formaldehyde titration. Plastein formation is a reversible process, and depends on the quantities of ferment, concentration of reacting substances, and reaction of the medium. The reversibility of the reaction can even be detected in very concentrated syrupy solutions. S. B. S.

**Synthetic Powers of the Organism of the Dog.** WILHELM STREFF (*Zeitsch. physiol. Chem.*, 1913, 84, 359—369. Compare A., 1911, ii, 1002; this vol., i, 419).—This is a reply to Abderhalden's criticism of the author's work. The death which follows feeding mice on nutriment boiled in alcohol is attributed to destruction of lipoids, and doubt is expressed whether mice possess the synthetic powers to construct these substances from simple cleavage products. W. D. H.

**Metabolism Experiments on Parathyroidectomised Dogs.** ISIDOR GEFENWALD (*J. Biol. Chem.*, 1913, 14, 363—367). After removal of the parathyroids, the excretion of phosphorus in the urine is lessened; there is no increase of phosphorus in the tissues; apparently it is retained in the body. This retention appears to be primary, and not secondary to the retention of sodium or potassium, or of both. In no experiments did the retention of the bases precede that of phosphorus. Whether the changes are the cause of tetany is questionable. W. D. H.

**The Carbohydrate-sparing Action of Alcohol.** O. TELLER, E. PRZYMNA, and ARNOLD DUNG (*Biochem. Zeitsch.*, 1913, 50, 236—245). The method of experiment was as follows. A human subject was kept on a carbohydrate-rich diet. A large quantity of dextrose or levulose was then ingested, and the respiratory quotient was determined at definite intervals afterwards, while the subject was kept in a state of rest. The results thus obtained were com-

pared with those where the experiment was carried out in a similar manner, but where alcohol was ingested in addition to a carbohydrate. After ingestion of 100 grams of dextrose, it was found that the respiratory quotient sank at first, but began to rise after half an hour, until after two hours it gradually rose to 1. After an interval, it gradually sank, until after four hours it reached the original value. Repeated doses of 100 grams of dextrose administered to a subject on carbohydrate-rich diet finally caused only a slight rise in the respiratory quotient. The sugar in this case was neither burnt, excreted as such, nor found in the blood-stream. Lævulose acted in a similar manner, but the action was somewhat more marked than that of dextrose. By repeated doses of 30 grams of levulose, the respiratory quotient could be maintained for a long time at 1. The general effect of the ingestion of alcohol with the sugar was to depress the respiratory quotient as compared with the control experiments without alcohol. The addition caused no change in the calories used up. In the first period, it was calculated that 70-100 mg. of alcohol were burnt per minute. The depression of the respiratory quotient is not due to the narcotic action of the alcohol, as this is uninfluenced by other narcotics, such as opium. The conclusion is therefore drawn that alcohol exerts a carbohydrate-sparing action in the metabolism.

S. B. S.

**Nitrogenous Metabolism.** EMIL ABIGERBALDEN and ARNO E. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **84**, 361-362).—Polemical. A reply to Grafe (this vol., i, 517).

W. D. H.

**Intermediary Metabolism of Amino-acids.** HENRY D. DAKIN (*J. Biol. Chem.*, 1913, **14**, 321-333).—Serine, cysteine, proline, ornithine, and arginine all yield large amounts of sugar in glycosuric dogs. Valine, leucine, *isoleucine*, lysine, histidine, phenylalanine, and tryptophan yield little or no sugar. Arginine is thus the only amino-acid with more than five carbon atoms which yields sugar, and in this case the ornithine moiety is responsible for the action. Amino-acids with branched chains yield little or no sugar. Proline is the only cyclic amino-acid which yields sugar readily: the opening of the ring is the first step in the breakdown. Phenylalanine, tyrosine, and tryptophan all contain an alanine side chain, but yield no sugar, although alanine itself does: this indicates that the side-chain is broken up.

Ornithine, lysine, arginine, proline, tryptophan, and diiodo-tyrosine do not yield acetoacetic acid in marked amounts when added to blood perfusing a dog's liver.

W. D. H.

**The Behaviour of Some Hydantoin Derivatives in Metabolism. II. 2-Thiohydantoins.** HOWARD B. LEWIS (*J. Biol. Chem.*, 1913, **14**, 245-256).—2-Thiohydantoin is toxic for rabbits; the toxicity is increased by the substitution of an alkyl group in the 4-position. 2-Thio-4-methylhydantoin is less toxic, and 2-thiohydantoin-4-acetic acid is not toxic in doses of 2 grams. 2-Thio-

4-methylhydantoin in fatal doses causes albuminuria in rabbits. The sulphur is not oxidised. W. D. H.

**Purine Metabolism. I. Uricolysis in the Human Subject.** ALONZO E. TAYLOR and WILLIAM C. ROSE (*J. Biol. Chem.*, 1913, 14, 419—422).—The nitrogen of milk and eggs was replaced by that of sweetbreads. The purine nitrogen of the urine was increased; this increase is due solely to uric acid. More than half the ingested nitrogen was, however, either destroyed in the alimentary tract before absorption, or was converted in metabolism into non-purine substances, presumably urea. W. D. H.

**The Utilisation of Ammonia in Protein Metabolism.** ALONZO E. TAYLOR and A. I. RINGER (*J. Biol. Chem.*, 1913, 14, 407—418. Compare this vol., i, 548). In dogs during inanition, and still more in diabetic dogs, ammonium carbonate given by the mouth led to a retention of nitrogen; given under the skin it was promptly eliminated. The administration of urea was followed by complete elimination of all the nitrogen. Ammonia given to man on a protein-free diet was retained to the extent of two-thirds. The presence of carbohydrates in the food is not a necessary factor in the retention of nitrogen from ammonia. It is suggested that the nitrogen is retained because of a reversible reaction that leads to combination with the  $\alpha$ -ketonic- or  $\alpha$ -hydroxy-acids to form amino-acids, which may be used in the synthesis or sparing of the body proteins. W. D. H.

**The Action of Completely Cleaved Nutriment on the Alimentary Canal.** OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1913, 84, 419—424).—Although it has been shown that animals can maintain nitrogenous equilibrium on protein food which is broken down to the simplest constituents, no note has hitherto been made on the effect of such diet on the alimentary canal itself. There are other factors, such as taste, consistence, etc., which influence digestion in addition to chemical composition. In the present research, however, in a dog with a duodenal fistula fed on two commercial specimens of such nutriment (crepton and hapant), no effect on the time of digestion in the stomach or on the amount of digestive juices secreted could be found, when compared with what occurs on a usual diet. These preparations were found to be well absorbed when administered by the rectum. W. D. H.

**The Preparation of Dry Animal Organ Material.** ALBRECHT KESSLER (*Zeitsch. physiol. Chem.*, 1913, 84, 354—358).—An elaborate apparatus is described which enables animal organs to be frozen solid by means of carbon dioxide snow, cut into small pieces, and dried below 65°. Colourless or reddish-grey powders are thus obtained from the original organs. E. F. A.

**The Relative Influence of Weak and Strong Bases on the Rate of Oxidations in the Unfertilised Egg of the Sea Urchin.** JACQUES LOEB and HANNOLOPH WASTENEYS (*J. Biol. Chem.*, 1913, 14, 355—362).—Weak bases, which are more efficient in causing

artificial parthenogenesis, are also more efficient in raising the rate of oxidation in the unfertilised egg cell. This lends support to the view that bases cause parthenogenesis by accelerating oxidation.

W. D. H.

**Chemistry of Embryonic Growth. I. Certain Changes in the Nitrogen Ratios of Developing Trout Eggs.** ROSS A. GORTNER (*J. Amer. Chem. Soc.*, 1913, 35, 632-644).—An account is given of a study of the nitrogenous constituents of trout eggs at various stages of development. It is probable that the egg does not lose any nitrogen before hatching, but afterwards it suffers a rapid loss, until in twenty-one days after hatching, 21.96% of the total nitrogen has disappeared. During its development into the fish, the egg loses 25.35% of its weight, of which 37.26% is due to non-protein matter (fats, etc.) and 62.74% to proteins, and simultaneously basic forms of nitrogen increase at the expense of the monoamino-acids. Urea and uric acid are not produced in any considerable quantity. The composition of the nitrogenous substances which disappear indicates that there is a selective utilisation of the nitrogen compounds by the developing fish. It is probable that some of the energy of development is derived from the shifting of the nitrogen ratios, and it is suggested that as the change from monoamino acids to basic nitrogen compounds proceeds the energy relations may perhaps be changed and heat liberated.

E. G.

**Chemical Differentiation of the Central Nervous System.**

**I. Comparison of the Brain of the Albino Rat at Birth with that of the Fœtal Pig.** (Miss) MARILYN L. KOCU (*J. Biol. Chem.*, 1913, 14, 267-279).—Estimation of the constituents of the brain of the rat at birth shows it to be as chemically undifferentiated as the brain of a 50-100 mm. length fetal pig. The correspondence is further supported histologically. If the nervous systems are assumed to be in corresponding states when motor control is obtained, and Donaldson's law is correct that the nervous system is in the same state at corresponding physiological ages, then the brain of the rat at birth should correspond chemically with the 160 mm. fetal pig brain. This was found to be the case.

W. D. H.

**Chemical Differentiation of the Central Nervous System.**

**II. A Comparison of Two Methods of Preserving Nervous-tissue for Chemical Examination.** WALTER KOCU and (Miss) MARILYN L. KOCU (*J. Biol. Chem.*, 1913, 14, 281-282).—The material was placed directly in 95% alcohol, and part was dried at 95°. The latter process was found to seriously affect the analyses, the most important change produced being a destruction of phosphatides; this was more marked in brains than in spinal cords.

W. D. H.

**Distribution of Nerves in the Heart.** (Miss) WINIFRED C. CLEGG and (Mrs.) ERIC M. TEEB (*J. Physiol.*, 1913, 46, 111-150).—After section of the auriculo-ventricular bundle in rabbit and cat,



pilocarpine and muscarine no longer inhibit ventricular activity; they act on the auricles as usual, and are antagonised by atropine; atropine has no effect on the ventricles. Under similar conditions adrenaline produces its normal augmentor effect on the ventricles. From this, it appears that the ventricle does not receive vagus fibres, and that the normal effect of the vagus on the ventricles is therefore indirect through the auricle; further, the ventricle must be supplied with sympathetic fibres, which reach it not only by way of the auriculo-ventricular bundle. W. D. H.

**Action of Certain Drugs on Isolated Strips of Ventricle.** (Miss) CONSTANCE LEETHAM (*J. Physiol.*, 1913, **46**, 151-158).—Experiments are recorded with isolated strips of ventricle which confirm the findings of Cullis and Tribe (see preceding abstract). W. D. H.

**Action of Dyes on the Isolated Frog's Auricle.** A. J. CLARK (*Proc. Physiol. Soc.*, 1913, xx; *J. Physiol.*, **46**).—The excised auricle and fibres of the frog's heart beat in Ringer's fluid for some hours. Neutral red dissolved in the fluid stains the muscular fibres red, but does not injure them. If the alkalinity of the fluid is increased, the fibres remain red as long as they exhibit activity, but when the concentration of alkali is sufficient to arrest activity, they turn yellow. This agrees with Warburg's observations on sea-urchin eggs, and supports the conclusion that normally animal cells are not permeable to hydroxyl ions. W. D. H.

**The Presence of Trimyristin and Cephalin in the Liver** ARMANDO FRANK (*Biochem. Zeitsch.*, 1913, **50**, 273-282).—The coagulated and dried ox liver was extracted by acetone, from which solution, on keeping, a crystalline substance separated, which was identified as trimyristin. The liver powder was then extracted with light petroleum. The extract thus obtained was dissolved in ether and precipitated with acetone. The precipitate was redissolved, filtered, and then reprecipitated with acetone, and this procedure was repeated many times. The substance was, in composition and properties, nearly allied to the cephalin isolated from brain by Thudichum and others. Experiments were carried out which tend to show that the so-called liver jecorin is cephalin contaminated with other substances, such as sugar. S. B. S.

**Estimation of Adrenaline.** THOMAS R. ELLIOTT (*Proc. Physiol. Soc.*, 1913, xv-xvii; *J. Physiol.*, **46**).—Many workers give adrenaline values which are too low owing to faulty extraction and estimation. At birth nearly all the adrenaline is in the outside paraganglia; in the adult the two suprarenals contain 8-9 mg. In septic conditions it may drop to a quarter of this value. Estimations may be made by the effect on arterial pressure, or by the new colorimetric reaction of Folin and Denis with phosphotungstic acid. The two work out practically the same, but the latter is much the simpler and quicker method. W. D. H.

**The Iodine and Phosphorus Contents, Size, and Physiological Activity of the Fetal Thyroid Gland.** FREDERIC FENGER (*J. Biol. Chem.*, 1913, 14, 397—495).—Functional thermogenic activity and the presence of iodine coincide in the fetal human thyroid as in extra uterine life. The amount of iodine during the last three months of fetal life is uniform in the various seasons. The fetal thyroid is relatively large, and contains more iodine and phosphorus per unit of body weight than those from mature animals. This is especially the case for females. Enlarged thyroid glands were found in small fetuses. The enlarged glands, as in the adult, contain less iodine and more phosphorus than the normal. Enlargement of the fetal thyroid is common, and is probably the consequence of insufficient supply or faulty assimilation of iodine on the part of the pregnant animal. W. D. H.

**The Changes in Metabolism Produced by the Extirpation of Thyroids and Parathyroids.** RAFFAELE PALADINO (*Biochem. Ztsch.*, 1913, 50, 497—507).—The experiments were carried out on dogs. The parathyroids and thyroids appear to exert a considerable influence on the phosphorus metabolism, for after extirpation the amount of phosphate excreted (chiefly in the form of phosphates of alkaline earths) increases to three times the normal amount. The amount of calcium excreted diminishes. There is no marked change in the nitrogen excretion. S. B. S.

**The Relation of the Corpus Luteum to Lactation.** CHARLES H. O'DONOGHUE (*Proc. Physiol. Soc.*, 1913, vi; *J. Physiol.*, 46).—In rabbits, if the rupture of the Graafian follicles in the ovary is followed by the formation of corpora lutea, there is also growth of the mammary glands, but there is no such growth if corpora lutea do not form. W. D. H.

**Biochemistry of the Female Genitalia. III. Enzymes of Ovary, Uterus, and Bladder in Sheep.** JACOB ROSENBLUM and TATISCO A. ENR-LERKOWICZ (*Biochem. Bull.*, 1913, 2, 233—235).—Lipase and amylase are more abundant in the ovary and uterine mucous membrane of pregnant than of non-pregnant sheep. Pregnancy has no effect on the acid-protease of either organ, but increases the alkali-protease. Bladder extracts contained lipase, amylase, and acid-protease, but no alkali-protease. W. D. H.

**Biochemistry of the Female Genitalia. IV. Absence of Certain Enzymes from the Human Chorion.** JACOB ROSENBLUM (*Biochem. Bull.*, 1913, 2, 236—237).—One chorion weighing 10 grams was examined. Extracts made with water and with glycerol were free from amylase, sucrase, maltase, lactase, lipase, peptidase, creptase, acid-protease, and alkali-protease. The enzymes of the placenta are either developed later, or originate from the maternal society (*decidua serotina*). W. D. H.

**The Effect of Small Variations in Concentration of Ringer's Solution on the Response of Isolated Plain Muscle.** HENRY H. DYLE (*Proc. Physiol. Soc.*, 1913, xix; *J. Physiol.*, 46).—By adding

salt in small amounts to Ringer's fluid in which plain muscle (uterus) is suspended, the response of the muscle to the anaphylactic reaction and to stimulant drugs is lessened or annulled. If the tonicity of the fluid is lowered by adding water, the responsiveness is increased. The effects are not due to specific ionic action, but are due to alterations in osmotic pressure; solutions of non-electrolytes produce the same effects.

W. D. H.

**Muscle Chemistry. VI. The Free Amino-acid Nitrogen Titratable by Formaldehyde and the Total Extractive Nitrogen in Muscular Tissue of Animals in a State of Inanition.** GIUSEPPE BEGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1913, **84**, 243-253).—In dogs to which water only was given for periods varying from twelve to twenty-five days, there was no change in the total nitrogen of the muscles, but there was a small increase in the total extractive nitrogen and in the nitrogen of free amino-acids. This change is not a progressive one, that is, it does not increase as the period of inanition increases. Confirmatory experiments on the octopus are also recorded.

W. D. H.

**The Lipins (Lipoids) of the Heart Muscle of the Ox.** JACOB ROSENTHAL (*J. Biol. Chem.*, 1913, **14**, 291-294).—Only about 4% of the ether and alcohol extract of heart muscle of the ox is composed of phospholipins (phosphatides), and practically no difference in this percentage was obtained on comparing the extractions carried out in the cold with those carried out at the boiling point of the solvent.

W. D. H.

**Origin of Fatigue.** GAETANO VIALE (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 253-256).—In prolonged muscular work quantities of water are eliminated in the sweat. This water comes from the blood, which in turn withdraws water from the tissues. When a certain point is reached, the necessary water is no longer forthcoming. This is evidenced by decreased secretion of sweat, and by increase in the amount of sodium chloride contained in it. The origin of fatigue is to be found in this removal of water, which causes accumulation of toxins in the blood and disturbs the regulation of the organism. In agreement with other workers, the author finds a decrease in red blood corpuscles and in haemoglobin in fatigue, and this is to be explained as being due to an accumulation of them in the organs.

R. V. S.

**The Behaviour of the Creatine of Muscle during Fatigue.** VITTORIO SCARFIDI (*Biochem. Zeitsch.*, 1913, **50**, 402-417).—In the muscular tissue of the frog and dog (and probably in all muscular tissue) creatinine does not exist as such in a preformed condition. Care must be taken to exclude high temperatures and acid in the process of its extraction from the tissues. Neither does creatine appear to be formed in frog's muscle during work; if it is formed it is either immediately removed or destroyed. Creatine shows certain variations in the quantity found, both in resting and

fatigued conditions, these variations being of about the same order of magnitude in both cases. It was not possible therefore to draw the conclusion that the creatine is formed as a result of work. It is, however, possible that during work creatine is used up, and new supplies are formed from degradation products of the muscle proteins. The condition of the circulation exerted no influence on the creatine metabolism in the frog during muscular work, as similar results were obtained when the circulation was intact, or entirely excluded.

S. B. S.

**The Effect of Adrenal Secretion on Muscular Fatigue.** WALTER B. CANNON and L. B. NICE (*Amer. J. Physiol.*, 1913, **32**, 44-60).—The experiments were performed on cats, rabbits, and dogs; a fatigue curve of a voluntary muscle was obtained by stimulating its nerve. Excitation of the splanchnic nerve increased the height of the muscular contraction. The question was whether this was due to the pouring out of adrenaline into the circulation, and this is answered in the affirmative; the adrenaline appears to act, however, not on the muscle directly, but by improving the circulation of blood through it. Previously reported favouring effects of adrenaline on voluntary muscles (mainly studied in cold-blooded animals) are capable of a similar explanation.

W. D. H.

**The Consumption of Fats in the Animal Organism.** G. LAFON (*Compt. rend.*, 1913, **156**, 1248-1250).—In order to determine the consumption of fat by the tissues, the author has estimated the amount of fat in the arterial blood and in the venous blood coming from the muscle, first in a state of repose, and then during activity. This has been done in the case of the horse and the ass, working on the muscle of the upper lip, activity being produced by mastication, and in the case of the dog on the muscle of a hind limb, the muscle being electrically excited. The results show that the fat is consumed directly, and to the same extent as dextrose, during the activity of the tissues, and in particular during muscular work. Muscles fatigued by electrical excitation contain less fat than fresh muscle.

W. G.

**Fluorine in the Animal Organism. I. Skin and its Appendages.** ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, **156**, 1347-1353).—Fluorine is to be found everywhere in the organs of plants and animals, but is specially concentrated in a few of them. This paper gives an account of the quantitative examination for fluorine of the skin, and such appendages as the hair, epidermis, nails, tooth enamel, etc., in the case of human beings, animals, birds, and fishes. In their fluorine content, the hair, down, fish-scales, nail, and tortoiseshell resemble the epidermic tissue, whilst the enamel of teeth and the horns differ from it widely, the former parts being rich and the latter poor in fluorine. The fluorine in skin itself appears to accompany the phosphorus and increase with it, for the same organs, without being proportional

to it. It is more abundant at the adult age in human than in animal skin, and diminishes in organs which are in process of decay, such as hair, teeth, etc., of old animals.

The method of estimation consists in incinerating the organ under examination, when dried, with 1 to 1.5% of calcium oxide, and the fluorine is estimated in the alkaline non-fused ash by a method already described (compare A., 1912, ii, 681, 805, 806). W. G.

**The Relation of Osmotic Pressure to Absorption Phenomena in the Dog-fish.** G. G. SCOTT and WILLEY DEXIS (*Amer. J. Physiol.*, 1913, **32**, 1-7).—Dog fishes, of which the spinal cord was largely destroyed, were immersed in various solutions (methylene-blue, boric acid, potassium iodide), and the material being prevented from entering the alimentary canal, the time was noted when they appeared in the blood, urine, etc. The gill membranes appear to be the main channel of absorption, and the physical laws of diffusion suffice to explain the results. W. D. H.

**The Action of Ultra-violet Rays on the Ear of the Rabbit Influence of Intensity. Intermittent Radiations.** VINCENZO MOYNIOT (*Compt. rend.*, 1913, **156**, 1268-1271. Compare this vol. i, 424).—As the intensity of the radiation increases, the time necessary for the ear to be subjected to it, to produce visible effect, diminishes. The amount of energy necessary to produce minimum visible reaction is practically constant for intensities varying from 4 to 100. If, instead of continuous radiation, the ear is subjected to intermittent treatment, the visible effect is produced when the sum of the short radiations is equal to the continuous radiation, providing that the intervals between the application of the light do not exceed forty-eight hours. W. G.

**Chemical Studies on Rhizostoma Cuvieri.** RICHARD W. ZEYNER (*Monatsh.*, 1913, **34**, 581-621).—If a jelly-fish of the above type is removed from water, a mucous substance is exuded which contains innumerable stinging threads; it causes an intense burning when cautiously placed on the tip of the tongue. The mucous substance easily undergoes decomposition; when precipitated by ammonium sulphate and redissolved by a very weak potassium hydroxide solution, acetic acid throws down a flocculent precipitate which dissolves readily in hydrochloric acid; when heated with this acid, a solution is obtained which reduces Fehling's solution and gives an osazone. The precipitate given by acetic acid contains no phosphorus, whilst the potassium hydroxide solution gives the biuret reaction. The stinging threads are very resistant, and contain very appreciable quantities of silicic acid. When the above mucous substance is allowed to dry on the clothes, the dust causes redness, irritation and acute catarrh, which persists for several hours. The substance to which irritation is due appears to be non-volatile; a careful examination of the mucous substance, however, reveals the presence of an alkaloidal substance.

[With F. AMSEDER.]—Specimens of the *Rhizostoma* var.

analysed, also the water in which one had lived and parts of the organism, the results are to be seen in the original.

The blue colouring matter (zoocyanin) present in *Rhizosoma (Cuvieri)* varies slightly in tone with the age of the specimen. The fresh aqueous extract is neutral, and the coloured substance is almost entirely precipitated by a 22–27% solution of ammonium sulphate, when it is obtained as a gelatinous mass; it was purified by washing and fractional precipitation with ammonium sulphate solution. The aqueous solution of the substance is turned brown on warming to 55° or on adding alcohol or acetone. Formaldehyde has no effect, but precipitates are obtained with phosphotungstic acid, phosphomolybdic acid, potassium bismuth iodide, potassium mercuri-iodide, and a solution of iodine in potassium iodide. It thus appears that the colouring matter is a protein substance, and the composition is in confirmation of this view. The colour was examined spectroscopically.

D. F. T.

**Analysis of Human Bile.** JACOB ROSENBLUM (*J. Biol. Chem.*, 1913, 14, 241–244).—An analysis of a specimen of fistula bile is given, and compared with others previously published. W. D. H.

**The Physiology of Secretion in the Kidney.** OTTO GÖNHEIM (*Zetsch. physiol. Chem.*, 1913, 84, 451–467).—Sodium chloride and dextrose are taken up by the surviving kidney at body temperature from solutions, and fixed in loose chemical union, which is dissolved at boiling heat. These combinations, as well as the secretion of these substances by the kidney, have a certain threshold, beneath which the kidney unites with none, and over it with considerable quantities. The chemical combination with the cell-constituents is a preliminary stage in secretion.

W. D. H.

**The Conditions Affecting the Formation and Excretion of Formic Acid. The Estimation of Formic Acid in Urine.** HENRY D. DAKIN, N. W. JASSEY, and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1913, 14, 341–354).—The formic acid in urine is partly endogenous. The effect of a number of substances on formic acid excretion was investigated, including amino-, hydroxy-, and saturated fatty acids. Special attention is called to the effect of inanition, which greatly reduces the amount excreted. The acid is largely increased when carbohydrates are given by the mouth or subcutaneously. Protein feeding is followed by a similar but smaller increase. Formic acid is regarded as a product of the intermediary metabolism of carbohydrates and proteins.

Formic acid is estimated in urine by saturating the latter with ammonium sulphate, extracting with ether, removing the formic acid from the ether by sodium carbonate, acidifying with phosphoric acid, distilling in a current of steam, adding mercuric chloride to the distillate, and weighing the calomel formed.

W. D. H.

**The Excretion of Nitrogen Subsequent to Ligation of Successive Branches of the Renal Arteries.** J. D. PILCHER (*J. Biol. Chem.*, 1913, 14, 389–395).—Ligaturing half the blood

supply of both kidneys causes no noticeable disturbance in renal function. Complete ligation of one artery, and one branch of the other (that is, shutting off three-quarters of the arterial supply), results in prostration, loss of weight, and an increase of excretion of nitrogen; the animals, however, recover gradually. One quarter of the kidney tissue is therefore able to do the work of the whole.

W. D. H.

**A Differential Chemical Study of Glucoses from a Case of Pancreatic Diabetes.** FREDERIC LANDOLFI (*Biochem. Bull.*, 1913, 2, 217-222).—The sugar is diabetic urine (one specimen examined) is regarded as a complex of many carbohydrates which can be separated by various treatments. Some of these are dextrinlike, and yield with phenylhydrazine "pseudo-osazones," which are resinous and have low melting points. The work is not yet completed.

W. D. H.

**A Modification of Diphtheria Antitoxin.** A. T. GLENNY (*J. Hygiene*, 1913, 13, 63-67).—Evidence is adduced that diphtheria antitoxin is of two kinds, which affect two kinds of the toxin, one of which is lethal, and the other of which produces the local reaction.

W. D. H.

**Presence of Propionic Acid in the Secretions of Rheumatic Persons.** WILLIAM EICHNER DE CONINCK (*Compt. rend.*, 1913, 156, 1272).—The urine of rheumatic patients, after a severe attack, has an odour recalling at the same time butyric and acetic acids, and from this urine the author has isolated propionic acid. This acid he has also found in the discharge from eczema sores on such patients.

W. G.

**The Action of Nitrites on the Body Temperature of Normal Rabbits, and on those Rendered Hyperthermic by Brain Stimulation.** EMANUEL KRAUSS (*Arch. exp. Path. Pharm.*, 1913, 72, 97-128).—The experiments show that nitrites, as stated by Jacoby, depress the body temperature. Further observations are necessary to explain this, and also why the inhalation of amyl nitrite acts much more markedly on rabbits in a state of hyperthermia.

W. D. H.

**Action of Nitrites on the Body Temperature of Rabbits.** CARL JACOBY (*Arch. exp. Path. Pharm.*, 1913, 72, 129-152).—Nitrite given in various ways (inhalation, subcutaneously, etc.) depresses the body temperature of rabbits, especially if they are rendered hyperthermic by stimulation of the brain. These compounds appear to act chiefly on the heat-regulating centres, and secondarily by influencing the calibre of the skin vessels.

W. D. H.

**The Action of Electrolytes on Paramoecium.** (Miss) HANBORN (*Am. J. Physiol.*, 1913, 46, 130-140).—Experiments were performed to determine the  $C_{50}$  limits fatal to *Paramoecium*. These of-

even "buffer" are constant for the various cultures used, and are different for different "buffers." The simple trivalent positive ions are more potent than the complex trivalent ions. The action of the former, although similar to that of increased  $C_m$ , is not explained by hydrolytic dissociation. The action of various ions on the changes of movement is described. The action of hydrogen and hydroxyl ions and of multivalent cations and anions may possibly be ascribed to the power they possess of conferring electric charges on colloidal materials.

W. D. H.

**The Mechanism of Histamine Action.** C. OEHME (*Arch. exp. Path. Pharm.*, 1913, **72**, 76—96).—Histamine (4 $\beta$  iminoethylglyoxaline) is a base which Barger and Dale separated from the intestinal mucous membrane (A., 1911, ii, 217), and is also formed by bacterial action from the intestinal contents (Mellanby and Twort, A., 1912, ii, 853). In minute doses it is fatal to rabbits, producing a great fall of blood pressure, and the other symptoms of anaphylactic shock. The lethal dose is larger if the injection is made into the mesenteric vein instead of into the systemic circulation; it is therefore possible that the liver may have some action in destroying the poison. Slow injection into the jugular vein also lessens its toxicity, and the question is discussed whether this is due to its being destroyed in the blood, or to its removal from the blood. No evidence of actual destruction in the blood itself was discovered, and only traces pass into the urine. When tested on the isolated uterus, the same difference as to whether the injection or addition to Locke's fluid is made rapidly or slowly is noticeable, as in the intact animal. The uterine tissues take up the drug, and this can subsequently be washed out. The question of its activity seems to be related mainly to the concentration.

W. D. H.

**The Urinary Elimination of Morphine Injected into an Unaccustomed Animal.** H. DORLENCOURT (*Compt. rend.*, 1913, **156**, 1338—1340. Compare Toizé, A., 1901, ii, 220; Bettink, A., 1905, ii, 546).—In the case of the rabbit the intramuscular injection of morphine hydrochloride to the extent of 0.15 gram per kilo. of body-weight is always followed by urinary elimination of the alkaloid as such. This elimination begins within an hour of injection, is at its maximum from the second to the fourteenth hour, and ends after seventy-two hours. The total elimination amounts to about 4% of the alkaloid injected, and only traces of diacetylmorphine could be detected in the urine. The animals employed had never previously had morphine, and received only one injection.

W. G.

**Influence of Some Derivatives of Quinoline and of Naphthaquinoline on the Elimination of Uric Acid.** RICHARDO CHIESA and RICCARDO LEZZATTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 305—311).—2-*p*-Methoxyphenylquinoline-1-carboxylic acid, C<sub>17</sub>H<sub>11</sub>O<sub>2</sub>N, forms yellow scales, m. p. 217°. 2-*p*-Dimethylamino



phenylquinoline-4-carboxylic acid,  $C_{18}H_{16}O_2N_2$ , forms ruby-red crystals, m. p.  $192^\circ$  (decomp.). 6-Amino-2-phenylquinoline-4-carboxylic acid,  $C_{18}H_{16}O_2N_2$ , has m. p.  $160^\circ$  (decomp.). 2-Phenyl- $\beta$ -naphthaquinoline-4-carboxylic acid gives a methyl ester, m. p.  $124^\circ$ . In the preparation of the acid, a dihydro-derivative,  $C_{20}H_{18}O_2N$ , is also formed; it has m. p.  $226^\circ$ . A yellow substance of acid properties and m. p.  $275^\circ$  also occurs in the preparation of 2-*p*-dimethylaminophenyl- $\beta$ -naphthaquinoline-4-carboxylic acid.

The authors have investigated the influence of these acids and of a number of others on the excretion of uric acid (compare Nicolai and Dorn, *Arch. Klin. Med.*, 1908, **93**, 331). There is no increase of uric acid after administration of 2-*p*-methoxyphenylquinoline-4-carboxylic acid, 2-*p*-dimethylaminophenylquinoline-4-carboxylic acid or 6-amino-2-phenylquinoline-4-carboxylic acid. A small increase (15—18%) occurs with 2-*o*-hydroxyphenyl- $\beta$ -naphthaquinoline-4-carboxylic acid. A greater increase (18—27%) is observed with 2-*p*-dimethylaminophenyl- $\beta$ -naphthaquinoline-4-carboxylic acid, 2-phenyldihydro- $\beta$ -naphthaquinoline-4-carboxylic acid, and with 2-phenyl- $\beta$ -naphthaquinoline. Great increases occur after administration of 2-phenylquinoline-4-carboxylic acid ("atophan") and 2-phenyl- $\beta$ -naphthaquinoline-4-carboxylic acid ("diapurine"). The increase is somewhat less with the latter substance, but it is better tolerated.

R. V. S.

**Poisoning by Acid.** GERTRUDE D. BOSTOCK (*Zeitsch. physiol. Chem.*, 1913, **84**, 468—477).—Subcutaneous injection of glycine in rabbits has no protective action against the fatal effect of acids given by the stomach. The simultaneous administration of ammonium acetate with the acid hastens death. In acid poisoning, the ammonia in the urine increases absolutely and relatively; there is also a rise in total urinary nitrogen. The increase in the ammonia is much greater if glycine or ammonium acetate is given at the same time.

W. D. H.

**Distribution of Ante mortem Administered Arsenic in the Human Cadaver.** JOHN B. EKFLEY (*J. Amer. Chem. Soc.*, 1913, **35**, 483—485).—The analysis of the corpse of a person who had died from arsenical poisoning showed the presence of the following percentages of arsenic (calculated as  $As_2O_3$ ) in the various parts of the body: Kidneys, 0.02466; stomach walls, 0.02273; liver, 0.00961; intestines, 0.00377; heart, 0.00125; thigh, 0.00039; toes, 0.00031; brain, 0.00012; spinal cord, a trace.

E. C.

**The Influence of the Intestinal Poisons (*p*-Cresol and Indole) on the Central Nervous System of Animals.** S. WLADECKO (*Ann. Inst. Pasteur*, 1913, **27**, 336—340).—Continued ingestion of small quantities of *p*-cresol and indole, which are formed by the action of putrefactive bacteria on protein degradation products in the intestine, have no visible action on the general health of the animal, as compared with control animals, as a result of the regressive changes in the blood-vessels of the brain. These

alterations, which are produced by the substances, are less marked in the case of guinea-pigs than of rabbits. They have also been observed in an experiment on *Macacus cynomolgus*. Small doses of *peresol* and indole also produce after repeated ingestion a slight destructive change in the cellular elements of the central nervous system. S. B. S.

### Chemistry of Vegetable Physiology and Agriculture.

**Tyrosinase from Two Enzymes.** MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 932—937).—By the symbiotic action of *Actinomyces* with a common soil bacterium, tyrosine in an agar plate culture is oxidised to melanin, which appears as black spots on the culture plate. Neither organism alone oxidised tyrosine to the same stage. Other species of *Actinomyces* produce blue, red, or yellow pigments, the simultaneous presence of certain varieties of hay bacteria being favourable in the case of blue and red. Dextrose, malates, and nitrates form the chromogeneous food in this case instead of tyrosine. It is considered that the *Actinomyces* produce homogentisic acid from tyrosine, and that the bacterium oxidises this acid to melanin. Plant tyrosinase (from *Euphorbia lathyris*) is a mixture of these two oxidising enzymes. E. F. A.

**The Formation of Lactic Acid by Acetic Acid Bacteria.** ALFRED OSTERWALDER (*Centr. Bakt. Par.*, 1913, ii, 37, 353—364). When inoculated into sterilised red or white wine, two acetic acid bacteria were found to bring about an increase in the amount of lactic acid. This change was observed in both fresh and fermented wines, and was not affected by the addition of sucrose, levulose, and malic and tartaric acids. The addition of alcohol was followed by an increase in the amount of lactic acid as well as of acetic acid. Malic acid was decomposed by the organisms, while a reduction in the amount of sucrose was accompanied by an increase in total acids, possibly by the formation of gluconic acid. The fermentation is probably without practical significance, since wines possessing a high acetic acid content are regarded as worthless, and those with little acetic acid would only contain traces of lactic acid as a result of fermentation by these organisms. H. B. H.

**Natural Variation of *B. acidilactici* with Respect to the Production of Gas from Carbohydrates.** J. A. ARKRIGHT (*J. Hygiene*, 1913, 13, 68—86). A bacillus of the *B. acidilactici* group isolated from urine occurred in two varieties, one of which formed gas from sugars and alcohols, and the other of which formed acid, but no gas. Their other characters (serum reactions, etc.) were identical. W. D. H.

**Biochemical Activity of *Bacillus lactis erythrogenes*.** MARY LOUISE FOSTER (*J. Amer. Chem. Soc.*, 1913, 35, 597—600).—An investigation of the action of *Bacillus lactis erythrogenes* on milk has shown that it is progressively catabolic, the proteins being ultimately converted into mono- and di-amino-acids. This proteolytic change is probably due to an enzyme. By precipitation with alcohol, a soluble ferment can be obtained, which decomposes the lactose with formation of formic and acetic acids, and this seems to indicate the presence of an intracellular enzyme, which is set free by the alcohol after it has destroyed the organism. These changes in the milk are accompanied by the production of a pigment, which causes a red to dull brown coloration, and can be extracted with amyl alcohol; it is extracellular, since its formation is dependent on the life of the organism. E. G.

**The Inhibitory Selective Action on Bacteria of Substances Related to Monochloroacetic Acid.** WILLIAM J. PENFOLD (*J. Hygiene*, 1913, 13, 35—48).—*B. coli* (Escherich) when grown on agar to which phenylacetic acid has been added, produces colonies which vary in size, but produce about the same amount of gas from dextrose. When the agar contains monochlorohydrin or sodium monochloroacetate, it throws off variants which ferment alcohol with gas formation, and sugars without gas formation. *B. lactis aerogenes* on monochlorohydrin agar gives rise to variants unable to ferment glycerol. In cases of inhibitory bacterial selection by chemical agents, a comparison of the surviving cells with the original strain indicates what portion or function of the cell is implicated in the cell's intoxication. The cellular enzymes, by virtue of their specific chemical affinities, may play a part in cell intoxication. Phenol, for instance, is rendered more germicidal by the addition of acids; in many media, the cell enzymes produce acids; hence it is probable that phenol selections of bacteria commonly result in the development of new strains with impaired fermenting powers. W. D. H.

**Alcoholic Fermentation.** ALEXANDER VON LEBEDEV (*Zeitsch. physiol. Chem.*, 1913, 84, 308).—Polemical (compare Kostytchev this vol., i, 323). E. F. A.

**Influence of Respiratory Chromogens on Alcoholic Fermentation.** VLADIMIR I. PALLADIN and S. D. LAVOV (*Bull. Acad. Sci. St. Petersburg*, 1913, 241—252. Compare this vol., i, 430).—The authors have made experiments to ascertain the cause of the influence exerted on the action of zymase by the oxidising processes due to respiratory chromogens. The yeast employed was treated by von Lebedev's method (*A.*, 1911, i, 218), and the chromogens were obtained from turnips, sugar-beets, or mushrooms.

The fermentation of expressed plant juices by killed yeast in a current of air is accompanied by oxidation of the respiratory chromogen of the juice to a pigment, which greatly retards the action of the zymase: the retardation is especially marked when

the juice is oxidised prior to introduction of the yeast. In the case of boiled juice, which is incapable of converting the pro-chromogen into chromogen and of oxidising the latter to pigment, alcoholic fermentation proceeds readily. Further, no retardation occurs when the unboiled juice is fermented in a stream of hydrogen, which prevents oxidation of the chromogen to pigment.

In cases where the fermentation is delayed, the proportions of alcohol and of carbon dioxide formed are affected to equal extents.

Consideration of these results and of modern views concerning the mechanism of fermentation renders it probable that, in the above experiments, the pigment withdraws the hydrogen liberated in the formation of the intermediate fermentation products and oxidises it, by means of atmospheric oxygen, to water. The absence of the hydrogen necessary for the subsequent synthesis of the alcohol renders the formation of the latter impossible. T. H. P.

**The Use of Ammoniacal Salts in Wine-making.** RENÉ MARCILLE (*Compt. rend.*, 1913, 156, 1336-1338).—An examination of some musts, which took several weeks instead of four or five days for complete fermentation, showed them to be deficient in ammoniacal nitrogen. On the addition of ammonium phosphate to the grape-juice, fermentation proceeded at the normal rate. Ammonium sulphate gives slightly better results than the phosphate, but care must be taken with respect to plastering. The wine obtained by the slow fermentation was normal in every respect. W. G.

**The Action of Cyclamine on Alcoholic Fermentation.** JOHAN LUNDBERG (*Arkiv. Kem. Min. Geol.*, 1913, 4, No. 32, 1-24).—The rate of fermentation at 30° of a sugar solution by means of yeast in the presence of cyclamine was followed by measuring the volume of carbon dioxide evolved (compare Sator, T., 1906, 89, 128).

Preliminary treatment of the living yeast with a pure solution of cyclamine has no effect on its power of fermentation; in the presence of sugar, however, the activity of the yeast is greatly diminished by the cyclamine. The action of the poison (cyclamine) thus depends on the physiological condition of the cell.

The amount of cyclamine necessary to poison the yeast is proportional to the quantity of the latter. Above a certain limit of concentration of cyclamine a further increase in quantity does not increase the velocity of poisoning.

It is probable that the poisoning is not a simple chemical reaction, but depends on the individual resistance of the cells.

The action of cyclamine on dry yeast depends only on the active yeast present, and not on the total quantity of dry material.

Even in very small concentrations cyclamine has no stimulating action on the yeast fermentation. T. S. P.

**A Ferment of Bitter Wines.** E. VOISENET (*Compt. rend.*, 1913, 156, 1181-1182. Compare A., 1911, ii, 915, 1127).—The ferment from a bitter wine develops in sterile or natural wines, or in wines partly deprived of their alcohol. Thus grown it presents all the

morphological characters of the ferment from the bitter wine. The author names it *Bacillus amaraerylus*. It attacks glycerol, giving acetaldehyde, and other products of the fermentation are carbon dioxide, hydrogen, ethyl alcohol, volatile acids, and lactic and succinic acids. It rapidly attacks mannitol and the sugars, acts moderately on dextrin, but does not ferment erythritol, dulcitol, or starch. The fermentation of the sugars, sucrose, lactose, maltose, dextrose, levulose, and galactose is complete in the presence of calcium carbonate.

W. G.

**Does the Ferment Causing Bitterness in Wine Consume Cream of Tartar?** E. VOISENET (*Compt. rend.*, 1913, 156, 1410—1412. Compare preceding abstract).—A determination of the tartaric acid in wine before and after it has become bitter shows no difference in the content. Further, if the *B. amaraerylus* is sown on different nutrient solutions containing cream of tartar, no difference can be detected in the tartaric acid content after three months' action.

W. G.

**Zymase and Reductase in their Mutual Relations.** SERGEI LYOV (*Ber. Deut. bot. Ges.*, 1913, 31, 141—147).—The first or one of the first stages in the alcoholic fermentation of dextrose is the withdrawal of two hydrogen atoms from the dextrose molecule. The hydrogen temporarily attached to the reductase is necessary for the normal course of fermentation.

An exact parallelism exists between the reducing and the fermentative energy of yeast; so that the reducing energy of yeast can be measured by its fermentative energy. The question arises whether reductase exists as a separate, individualised ferment, or whether the reducing properties do not more probably belong to a single, if complicated, fermenting apparatus usually termed zymase?

N. H. J. M.

**Sugar-free Fermentations of Stereoisomerides.** PAUL MAYER (*Biochem. Zeitsch.*, 1913, 50, 283—287).—Hydroxyfumaryl acid, like the corresponding hydroxymaleic acid, undergoes fermentation with yeast, yielding carbon dioxide and acetaldehyde, which was isolated in the form of the *p*-nitrophenylhydrazone.

S. B. S.

**Replacement of Zinc by Uranium in the Culture of *Aspergillus niger*.** CHARLES LÉPOTIERRE (*Compt. rend.*, 1913, 156, 1179—1181.\* Compare this vol., i, 326, 327).—Uranium, like cadmium and glucinum, can replace zinc in the medium for the culture of *Aspergillus niger*. The weight of crop is normal if the amount of uranium in the form of nitrate is less than 1 in 5000; there is, however, a considerable retardation in attaining the maximum. Sporulation takes place if the amount of uranium is less than 1 in 10,000, but is checked by 1 in 5000. The addition of uranium to media containing zinc produces a marked retardation in growth, but the crop finally attains its normal maximum weight. The uranium is in all cases fixed by the plant.

W. G.

**Tannic Acid Fermentation. I.** LEWIS KNUDSON (*J. Biol. Chem.*, 1913, **14**, 159—184).—Tannic acid is toxic to many fungi in low concentrations. *Aspergillus niger* is a more vigorous fermentative organism than *Penicillium*. Fermentation is more rapid in the gall-nut infusion than in a synthetic solution, in which tannic acid was the only source of carbon. Certain organic compounds in the infusion protect the gallic acid to some extent. The addition of 5% of sugar did not protect the gallic acid, but simply increased the growth; 10% protected the gallic acid entirely. Fermentation can take place under anaerobic conditions, and 1 mg. of mycelium can effect the transformation of 2.7 grams of tannic acid in ten days. The presence of 10% of sugar does not inhibit the secretion of tannase by *Aspergillus niger*, but it does do so to some extent in *Penicillium*. This enzyme is secreted into the culture solution by submersed mycelium as well as by surface growth. There is no evidence that tannic acid is used directly; it is first transformed into gallic acid. W. D. H.

**Tannic Acid Fermentation. II. Effect of Nutrition on the Production of Tannase.** LEWIS KNUDSON (*J. Biol. Chem.*, 1913, **14**, 185—202).—There is a progressive increase of tannase in *Aspergillus* and *Penicillium* with increased concentration of tannic acid in Czapek's solution containing 10% sugar. In a full nutrient solution containing 2% tannic acid as a source of carbon, the addition of sucrose decreases the secretion of tannase. *Aspergillus* secretes more tannase (or more active tannase) per unit weight than *Penicillium*. The production of the enzyme is stimulated in both moulds by gallic and especially by tannic acids. W. D. H.

**The Catalytic Action of Light on the Germination of Seeds.** ERNST LEHMANN (*Biochem. Zeitsch.*, 1913, **50**, 388—392).—Experiments carried out with the seeds of *Epilobium hirsutum* show that in water and in the dark they only germinate very slightly, whereas under otherwise the same conditions 98—100% germinate when exposed to light. The same effect as that produced by light can also be attained by treatment in the dark with solutions of proteolytic ferments, such as papayotin and trypsin, and by low concentrations of acids (0.05*N*-hydrochloric acid). It appears, therefore, as if light acts catalytically in "mobilising" the proteins of the seeds. S. B. S.

**Influence of Cancer Extracts on the Growth of Lupine Seedlings.** JACOB ROSENBLUM (*Biochem. Bull.*, 1913, **2**, 229—232).—The extracts had no deleterious effects; but, on the contrary, growth was accelerated; this may be due to inorganic salts. W. D. H.

**The Action of Poisonous Substances in Different Concentrations on Seeds. The Biochemical Action of Very Concentrated Solutions.** V. ARCHONOVSKI (*Biochem. Zeitsch.*, 1913, **50**, 233—244).—The action of the following substances was investi-

gated: formalin, sulphuric acid, and silver nitrate. The seeds were soaked in varying concentrations in water of these substances for varying periods, then washed, and allowed to germinate under sterile conditions. The apparatus for carrying out these various operations is described and figured in the text. The number of seeds (pea-seeds) which germinate, and the percentages which start germinating in given times, were ascertained. The toxicity of these substances increases as the concentration is increased up to a certain optimal point. Further increase in the concentration beyond this point diminishes the toxicity. The causes of this phenomenon are discussed by the author. S. B. S.

**Anaerobic Respiration of Various Seed Plants.** S. KOTYTSCHNY (*Ber. deut. bot. Ges.*, 1913, 31, 125—129).—Experiments on the amounts of carbon dioxide produced by different plants during anaerobic respiration are described. The ratio  $\text{CO}_2/\text{EtOH}$  varied from 100/100 to 100/0.

It seems to be typical of leaves that about half the carbon dioxide is produced by zymase fermentation. Potato tubers produced only traces of alcohol, if any at all, and thus resemble mushrooms, which, however, contain no carbohydrates.

The results obtained support the view that, in most cases, anaerobic respiration is not identical with zymase fermentation. As a rule, zymase fermentation takes place at the same time.

N. H. J. M.

**The Evolution of Mineral Substances and Nitrogen in Some Annual Plants.** GUSTAVE ANDRÉ (*Compt. rend.*, 1913, 156, 1161—1167. Compare this vol., i. 233).—An extension of the above study to the case of the common flux, spurrey, and *Camelina sativa* shows that, for these three examples of different families of plants, all the mineral elements, as well as the total nitrogen, steadily increase in weight to the time of complete maturity. W. G.

**Experiments with Sterile Cultures of Higher Plants.** IVAN SCHULOV (*Ber. Deut. bot. Ges.*, 1913, 31, 97—121).—The phosphoric acid of lecithin is not assimilated by maize and peas. Phytin is utilised by peas as source of phosphoric acid.

The roots of maize and peas excrete considerable amounts of reducing sugars; maize also excretes malic acid.

Young plants, supplied with ammonium nitrate, take up more ammonia than nitrate; later on the two forms of nitrogen are utilised in about equal amounts, whilst subsequently chiefly nitric nitrogen is taken up by the plant. The physiologically acid reaction initially produced is undoubtedly of importance in the assimilation of phosphates insoluble in water.

The employment of ammonium nitrate causes an increased secretion of organic acids by the roots, and a greater secretion of sugars. N. H. J. M.

**Dry Heating.** CARL THOMAE (*J. pr. Chem.*, 1913, [ii], 87, 423—424. Compare A., 1911, ii, 920; this vol., i. 326, 327).—A

further note on the isolation of the fatty and waxy constituents from plant and animal matters by dry distillation, preferably under diminished pressure. Leaves, pine-needles, blossoms, hay, straw, hair, egg-shells, feathers, wood, and articles manufactured from them, such as cloth, paper, linen, leather, cigars, and wadding, all yield a fat or wax on distillation.

Filter paper and linen gave a white, crystalline wax. F. B.

**Localisation of Betaine in Plants.** VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1913, 37, 385—390).—The greatest amount of betaine was found in the leaves, especially in young leaves. Leaves of *Amarantus* contained 2.18, and the roots only 0.48% of betaine. The dry matter of sugar beet-roots contained 0.95 to 1.20%, whilst the leaves contained 2.62%. Beet seeds, without husks, contain only traces of betaine; in seeds of *Chenopodium foliol.*, no betaine was found. N. H. J. M.

**Chemistry of the Floral Pigments.** P. Q. KEEGAN (*Chem. News*, 1913, 107, 181—182).—The colour of blue flowers (gentian, campanula, centaurea, etc.) is attributed to the presence of caffeotannin, the only known tannin, except gallotannin, which yields blue oxidation compounds with bases, since it is related to styrene and cinnamic acid. It is doubted whether the presence of an inorganic base is necessary for the production of a blue colour. N. H. J. M.

**Chemical Examination of *Diosma anomala*.** FRANK TOLIN and WILLIAM J. S. NAUSTON (*Pharm. J.*, 1913, [iv], 36, 694—696).—The material employed for this investigation consisted of the entire dried plant of *Diosma anomala*, Sond., which had been specially collected in South Africa.

An alcoholic extract of the plant, when distilled in a current of steam, yielded a small amount of an essential oil, b. p. 130—200°; ordinary pressure. The portion of the extract which was soluble in water yielded a small amount of a colourless, crystalline *glucoside*, m. p. 243°, which appeared to possess the formula  $C_{19}H_{35}O_{17}$ , and a large quantity of a yellow, amorphous, deliquescent product, which, when hydrolysed with alkali, gave 3:4-dihydroxycinnamic acid. The aqueous liquid contained, in addition, a quantity of sugar which yielded *d*-phenylglucosazone, m. p. 218°.

The portion of the extract which was insoluble in water formed a dark-coloured, resinous mass. It consisted largely of amorphous products, some of which gave 3:4-dihydroxycinnamic acid on hydrolysis, and a small amount of an amorphous alkaloid was also present. The following definite substances were, however, obtained from the resin: (1) hentriacontane,  $C_{31}H_{64}$ , m. p. 68°; (2) a *phytosterol*,  $C_{27}H_{46}O$ , m. p. 159° (*acetyl* derivative, m. p. 133°), which seems to be a lower homologue of stigmasterol; (3) possibly myricyl alcohol; (4) phytosterolin; (5) palmitic, stearic, arachidic, cerotic, and melissic acids, together with some unsaturated acids, which appeared to consist chiefly of a compound,  $C_{16}H_{32}O_2$ . H. W.



Occurrence of Gentiopicroin and Gentianose in the Fresh Roots of *Gentiana cruciata*, L. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 7, 392—395).—Gentiopicroin and gentianose have been isolated in a crystalline condition from the roots of this species. (compare A., 1913, i, 149, 434). T. A. H.

Development of Fat in the Black Walnut (*Juglans nigra*). II. FRANK M. McCLENAHAN (*J. Amer. Chem. Soc.*, 1913, 35, 485—493).—In continuation of the work on this subject (A., 1909, ii, 924), analyses have been made of the ovule of the black walnut at various stages of its development. The fat accumulates rapidly up to a certain point, and afterwards increases but slowly. During the early period of development, the fat is waxy in character, but subsequently becomes liquid. In the very young ovule, phosphatides are greatly in excess of fat, but later their relative importance becomes insignificant. The young ovule contains a large proportion of potassium, but this decreases as the fruit approaches maturity. High percentages of calcium, magnesium, and phosphorus are also present during the early life of the ovule, but are relatively unimportant in the later stages. E. G.

The Anti-toxic Rôle of Calcium with Respect to Some Nutritive Salts in the Culture in Liquid Medium of Peas and Lupine. (Mlle.) C. ROBERT (*Compt. rend.*, 1913, 156, 915—918).—A comparison of the growth of seedlings of peas and lupins grown on: (a) distilled water, (b) solutions containing 500 mg. of calcium sulphate per litre, (c) solutions containing one of the usual nutrient salts in corresponding strength, (d) solutions, being a combination of (b) and (c). The results show that, with the strength used, calcium is not toxic, but very considerably favours the development of the young plants. The salts of magnesium, potassium, and ammonium are toxic at the concentration used, but the addition of a calcium salt suppresses this toxicity. The development in mixtures of salts of potassium, magnesium, or ammonium with the calcium salt is the same as when the calcium salt alone is used; thus, in the early days of its growth, the salts of these three metals do not seem to act as nutrients to the plant. The white lupin is more sensitive to the toxic action than the pea, very small quantities of potassium salts sufficing to arrest all development. W. G.

Nutritive Value of Maize Proteins. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxxi—xxxii; *J. Biol. Chem.*, 14).—About one-third of the proteins in maize consists of glutelin, which yields all the amino-acids found in most proteins. Zein causes rapid decline in weight, but may be made of greater value by adding tryptophan or other proteins. Gliadin suffices for maintenance, but not for growth. Glutelin is adequate for growth also. W. D. H.

**Cotton-seed Meal Intoxication. I. Pyrophosphoric Acid.** WILLIAM A. WITHERS and BURTON J. RAY (*J. Biol. Chem.*, 1913, **14**, 53—58).—The results indicate that pyrophosphoric acid is not the cause of the toxicity of cotton-seed meal. W. D. H.

**Accumulation of Nitrogen in the Soil by means of Micro-organisms.** JOSEF DVOŘÁK (*Zeitsch. landw. Vers. Wesen. Oesterr.*, 1912, **15**, 1077—1121).—A detailed account of numerous experiments based on the observations of Stoklasa (A., 1911, ii, 429) and others on the assimilation of nitrogen (atmospheric or otherwise) by plants, and the micro-organisms of the soil.

The influence of various organic substances is studied, and the conclusions arrived at that the ammonium ion is as readily absorbed as the nitrate ion, and that acid soils exhibit the least, and those with a neutral or alkaline reaction the highest, biological absorption. F. M. G. M.

**Fixation of Nitrogen by So called Zeolites.** GEORG WIEGNER (*J. Landw.*, 1913, **61**, 11—56).—Experiments were made to ascertain whether the ammonium fixed by zeolites in soils, or any portion of the ammonia, is rendered unavailable to plants. With regard to the amount of ammonia fixed by 100 grams of permutite it is shown that this varies according to the concentration of the ammonia in the solution.

Pot experiments are described in which oats followed by buck-wheat were manured with ammonium sulphate, without and with calcium zeolite in different amounts, and with ammonium zeolite both without and with calcium zeolite.

The results showed that addition of calcium zeolite increased the dry produce, and did not diminish the nitrogen. With large amounts of nitrogen applied as manure, the nitrogen was better utilised in presence of zeolites, possibly owing to losses in the pots without zeolites.

There can be no question of the permanent fixation of a definite and constant amount of ammonia by zeolites, as the amount which is fixed depends on the concentrations, which are variable. The changes are sometimes favourable and sometimes unfavourable to the plants. N. H. J. M.

**Action of Histidine and Arginine in Soils.** J. J. SKINNER (*Biol. Zentr.*, 1913, **42**, 213—214; from *Proc. 8th Internat. Cong. Appl. Chem.*, 1912).—Histidine and arginine, which are produced in soils as primary cleavage products of proteins, are favourable to the growth of plants except when large amounts of nitrates are present, when they have no appreciable effect. Like creatine and creatinine, both substances can take the place of nitrates. N. H. J. M.

**Influence of Sodium Carbonate and the Imperviousness of the Soil on the Growth of Plants.** JOHN W. LEATHES (*Biol. Zentr.*, 1913, **42**, 213; from *Proc. 8th Internat. Cong. Appl. Chem.*, 1912). The result of pot experiments in which alkali soils received

calcium sulphate in amounts sufficient to reduce the sodium carbonate from 0.06 to 0.01% failed to show any appreciable change in the physical properties of the soil. When the sodium carbonate was partly neutralised with calcium sulphate, 33% of the seeds germinated, the best results being obtained with rice and wheat. When the imperviousness of the soil was removed by addition of sodium chloride, 16% of the seeds germinated, but the plants did not rise. N. H. J. M.

**The Effect of Ignition on the Solubility of Soil Phosphates.** CHARLES B. LIPMAN (*J. Ind. Eng. Chem.*, 1912, 4, 663).—An account of the analysis of five typical soils, as a result of which the author draws the conclusion that the observation of Fraps (*A.*, 1912, ii, 87), that ignition increases the solubility of the phosphates in minerals, does not apply to soils where ignition appears to definitely decrease the solubility of the phosphates; and it is suggested that the increased solubility noted in minerals may be due to mechanical changes induced by heat, which, in disintegrating the particles, increase the amount of surface available for attack by acids.

F. M. G. M.

**Zinc as Catalytic Manure.** MAURICE JAVILLIER (*Biol. Zentr.*, 1913, 42, 215; from *Proc. 8th Internat. Congr. Appl. Chem.*, 1912).—Field experiments in which oats, maize, rye, clover, and peas received from 1 to 10 kilos. of crystallised zinc sulphate per hectare. The best results were obtained with maize, which always showed increased production under the influence of zinc sulphate, whilst the other plants gave irregular results.

Laboratory experiments were made with *Aspergillus niger*, showing the effect of zinc on the assimilation of carbohydrates, nitrogen, and minerals, and on the composition of the plant. N. H. J. M.

**Aluminium Sulphate as Catalytic Manure.** GABRIEL BERTRAND and HENRI AGELION (*Biol. Zentr.*, 1913, 42, 215; from *Proc. 8th Internat. Congr. Appl. Chem.*, 1912).—Small amounts of aluminium sulphate (2 mg. per kilo. of soil) increased the yield of barley 18%, or 17% calculated on the dry matter. With 4 mg., the dry produce was not increased, whilst there was a gain in the fresh produce.

N. H. J. M.

**Employment of Manganese as Catalytic Manure.** GABRIEL BERTRAND (*Biol. Zentr.*, 1913, 42, 214; from *Proc. 8th Internat. Congr. Appl. Chem.*, 1912).—In pot experiments with peas and barley it was found that addition of manganese sulphate increased the yield by 10–20%. Field experiments gave similar results, oats being increased 9.5%, by 60 kilos. of manganese sulphate per acre, peas 20% by 30 kilos., colza 18%, and clover 15% by 40 kilos. of manganese sulphate. The most suitable amounts of manganese sulphate are 30 to 50 kilos. of the anhydrous salt per hectare. N. H. J. M.

# CONTENTS.

## PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY

	PAGE
LXXVIII.—The Action of Tartaric Acid on Tin in the Presence of Oxygen. By ALFRED CHASTON CHAPMAN . . .	775
LXXIX.—Some Double Salts with Acetone of Crystallisation and the Crystallisation of Silver Iodide, Silver Bromide, and Cuprous Iodide. By JAMES ERNEST MARSH and WILLIAM CLAUDE RHYMES . . . . .	781
LXXX.—Notes on the Determination of the Electrical Conductivity of Solutions. By HAROLD HARTLEY and WILLIAM HENRY BARRETT . . . . .	786
LXXXI.—The Preparation of Conductivity Water. By ROBERT BOURDILLON . . . . .	791
LXXXII.—The Reaction between Ferric Salts and Thiocyanates. By JAMES CHARLES PHILIP and ARTHUR BRANLEY . . .	795
LXXXIII.—Non-aromatic Diazonium Salts. Part I. Antipyrinediazonium Salts and their Azo-derivatives. By GILBERT T. MORGAN and JOSEPH REILLY, B.A., B.Sc., A.R.C.Sc.I. . . . .	808
LXXXIV.—The Constitution of the Anhydro-bases derived from Tetrahydroberberine Alkyl Hydroxides. By FRANK LEE PYMAN . . . . .	817
LXXXV.—Optical Activity and Enantiomorphism of Molecular and Crystal Structure. By THOMAS VIVOND BARKER and JAMES ERNEST MARSH . . . . .	837

LXXXVI.—The Preparation of Pure Bromine. By ALEXANDER SCOTT . . . . .	1468 847
LXXXVII.—The Application of Hofmann's Reaction to Dialkylacetamides. By FRANK LEE PYMAN . . . . .	852
LXXXVIII.—Constitution of Aliphatic Diazo-compounds. By MARTIN ONSLOW FORSTER and DAVID CARDWELL . . . . .	861
LXXXIX.—The Conversion of Sodium Hydrosulphide into Sodium Monosulphide. By JOHN SKEATH THOMAS and ALEXANDER RULE . . . . .	871
XC.—The Absorption Spectra of Some Derivatives of the Nitroaminophenols in Relation to their Constitution. By RAPHAEL MELDOLA and JOHN THEODORE HEWITT . . . . .	876
XCI.—The Carbinol-Ammonium Base Isomerism in Connexion with Azomethine Bases. Part I. Derivatives of Cinnamylidene- <i>p</i> -toluidine. By CHARLES KENNETH TINKLER . . . . .	885
XCII.—The Constitution of Oxadiazole Oxides (Furazan Oxides or Dioxime Peroxides). By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE . . . . .	897
XCIII.—Naphthathioxin and <i>iso</i> Naphthathioxin. By THOMAS JOSEPH NOLAN and SAMUEL SMILES . . . . .	901
XCIV.—Studies of Dynamic Isomerism. Part XIV. Successive Isomeric Changes in Camphorcarboxylamide and Camphorcarboxypiperidide. By THOMAS MARTIN LOWRY and WALTER HAMIS GLOVER . . . . .	913
XCV.—Quinonoid Addition as the Mechanism of Dyestuff Formation. By ARTHUR GEORGE GREEN . . . . .	925
XCVI.—Influence of Increase of Initial Temperature on the Explosiveness of Gaseous Mixtures. By ALBERT PARKER, B.Sc. . . . .	934
XCVII.—Allylamine Derivatives. By WILHELM GLEUD, Ph.D. . . . .	940
XCVIII.—Experiments on the Synthesis of <i>apo</i> Morphine. By FRANCIS WILLIAM KAY and ANÉ PICTET . . . . .	947

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

## PART I.

*Organic Chemistry.*

	PAGE
ISIRATI (CONSTANTIN I.) and C. TEODorescu. Some Data of the Solubility of Metallic Copper in the Different Fractions Obtained by the Distillation of Crude Petroleum . . . . .	i, 437
LEBEAU (PAUL) and A. DAMIENS. The Composition of Illuminating Gas . . . . .	i, 437
STERNER (RICHARD). Mechanism of the Transformation of Stereoisomeric Ethylene Compounds . . . . .	i, 437
FOMIS (W.) and M. SOCHANSKI. Elimination of Water from Pinacolyl Alcohol and on Tertiary Butylethylene . . . . .	i, 438
BADISCHE ANILIN- & SODA-FABRIK. Preparation of $\beta\gamma$ -Dimethyl- $\Delta^2$ -butadiene . . . . .	i, 438
BADISCHE ANILIN- & SODA-FABRIK. Preparation of Dioléfines . . . . .	i, 438
LEBEAU (PAUL) and MARIUS PICON. The Action of Monosodioacetylene on the Alkyl Iodides. Preparation of True Acetylenic Hydrocarbons . . . . .	i, 438
CHABLAY (E.). Preparation of Primary Alcohols by Reduction of the Esters with Absolute Alcohol and Sodium-ammonia . . . . .	i, 438
MARING (HUGO). New Methods of Spirit Rectification . . . . .	i, 439
GORSKI (ALEXANDER I.). $\beta\gamma$ -Dimethylbutan-2-ol . . . . .	i, 439
DEMIDOV (NICOLAI J.). New Data Concerning the Oxide of Pentamethylene Glycol . . . . .	i, 439
MAMELET (Mme.) and H. MARCELET. Development of Heat on Mixing Ether and Chloroform . . . . .	i, 440
STRECKER (WILHELM). The Constitution of Sulphurous Acid . . . . .	i, 440
GOESNER DE CONINCK (WILLIAM) and ALBERT RAYNAUD. Decomposition of Formates . . . . .	i, 440
BOMBROUX (FERNAND). Catalytic Esterification in Dilute Solutions: Preparation of Ethyl Acetate . . . . .	i, 440
MARCUSSON (JULIUS). The Hydrolysis of Fats . . . . .	i, 441
BOMER (ALOIS). Glycerides of Fats and Oils. IV. The Mixed Glycerides of Palmitic and Stearic Acids Obtained from Lard . . . . .	i, 441
BOMER (ALOIS) and R. LIMPRICH. Glycerides of Fats and Oils. V. Nomenclature of Mixed Glycerides and the Synthesis of $\alpha$ -Distearin and $\beta$ -Palmitylidistearin . . . . .	i, 442
FORIN (SERGEI A.). China Oil . . . . .	i, 442
FORIN (SERGEI A.). Behaviour of Certain Unsaturated Acids Towards Selenous Acids . . . . .	i, 442
BAUR (EMIL). Formation, Decomposition, and Transformation of Glycollic Acid . . . . .	i, 443
ALEXANDROV (DIMITRI K.). Method of Preparing Ethyl $\gamma$ -Chloroacetate . . . . .	i, 443
TAYLOR (HERMAN J.). Action of Oxalyl Chloride on Several Organic Derivatives . . . . .	i, 443
COLANI (A. E.). Solubility of Thorium Oxalate . . . . .	i, 444
McMASTER (LEROY). Preparation and Properties of the Ammonium Salts of Some Organic Acids . . . . .	i, 444

	PAGE
MOROSCHKINA (O. I.). Crystalline Form and Optical Properties of Magnesium Malate	i, 144
VIGUIER (PAUL L.). Tetrolaldehyde ( $\Delta^4$ -Butinal) and Some of Its Derivatives	i, 144
LASSIEUR (A.). Catalytic Hydrogenation of Acetone	i, 144
BLAISE (EDMOND E.). Migration of the Chlorine in the Halogenated Ketones	i, 144
FISCHER (EMIL) and KARL ZACH. Reduction of Acetobromoglucose and Similar Substances	i, 145
PLIMMER (R. H. ADAMS) and HAROLD J. PAGE. Phytin	i, 145
ALBERDA VAN KREKSTEIN (WILLIAM) and JAN J. BLANKSMA. Transformation of <i>L</i> -Arabinose into <i>L</i> -Ribose	i, 145
DURIEUX (O.). Action of Hydrogen Peroxide and Ferric Chloride on Starch	i, 145
TANAKA (YOSHIO). Starch of Glutinous Rice and Its Hydrolysis by Diastase	i, 146
OST (HERMANN). The Acetolysis of Cellulose to Dextrose Acetate	i, 146
Tedesco (IL.). Nitrocellulose	i, 147
LEAVITT (SHERMAN). Soil Humus	i, 147
MEISENHEIMER (JAKOB). Action of Hypochlorous Acid on Tertiary Amines	i, 147
URBAN (KARL). Preparation of Betaine from Molasses Residues	i, 149
GASASSISI (DOMENICO). Chemical Reactions Brought About by Sunlight	i, 149
LECHES (HERMANN) and JOSEPH E. BREWSTER. Synthesis of the Natural Hydroxyproline Present in Proteins. Pyrrolidine Derivatives. IV.	i, 149
ABDERHALDEN (EMIL) and ARTHUR WEIL. A New Amino-acid of the Composition $C_6H_{12}O_2N$ Obtained by the Total Hydrolysis of the Proteins of the Nerve Substance	i, 150
RADLERGER (LEOPOLD). Compounds of Guanylecarbamide and Guanyleguanidine with Dextrose	i, 150
LINDBOLM (HJALMAR). Action of Sulphuric Acid on Dicyanodiamide. Correction	i, 151
WERNICKE (RAÛL). Colour Changes in Solutions of Cobaltous Thiocyanate	i, 151
VENDITTOI (DOMENICO). Reduction of Sodium Nitroprusside by Hydrogen Sulphide	i, 151
DEMIANOV (NICOLAI J.) and M. DOJARENKO. Vinylcyclopropane and its Derivatives	i, 151
WALLACE (OFFO) [with L. AUGSPURGER and HANS SCHUBACH]. Terpenes and Etheral Oils. CXIV. Alicyclic Unsaturated Hydrocarbons	i, 152
BADISCHER ANILIN- & SODA-FABRIK. Preparation of Partly Hydrogenised Cyclic Hydrocarbons	i, 153
KUNCKEL (FRANZ) [with KURT ERAS, ALFRED HILDEBRANDT, and EMIL MÜLLER]. Derivatives of Phenylacetylene, Methoxyphenylacetylene, and Allied Compounds	i, 153
FABERFABRIKEN VORM. FRIEDR. BAYER & CO. Preparation of Sulphonic Acids of the Benzene and Naphthalene Series	i, 155
SPRAY (FRITZ). $\Delta^1$ -Dihydronaphthalene	i, 155
MEYER (KURT H.) and KARL ZAHN. Halogen Compounds of Anthracene	i, 155
FABERFABRIKEN VORM. FRIEDR. BAYER & CO. Preparation of $\alpha$ -Substituted Derivatives of Acetoacetanilide and Their Homologues	i, 156
LANGENSCHIEDT (F.). The Manufacture of Tetranitromethylaniline	i, 157
FABERFABRIKEN VORM. MEISNER, LECHE & BRÜNING. [Preparation of 4-Chloro-2-(4-Iaminophenyl)]	i, 157
FABERFABRIKEN VORM. FRIEDR. BAYER & CO. Preparation of Dialkylaminofornic Esters	i, 157
FABERFABRIKEN VORM. MEISNER, LECHE & BRÜNING. Preparation of Aromatic Schreyer-compounds	i, 158
WEINLAND (RUDOLF F.) and KARL HINDEL. Iron Compounds of Phenols. IV.	i, 158
AGOSTINELLI (CLAUDIO). Some Additive Products of Styphnic Acid	i, 159

# CONTENTS.

v

	PAGE
SACCHARIN-FABRIK AKTIENGESELLSCHAFT VOHM, FAHLBERG, LIST & Co. Preparation of 2:3-Dihydroxytoluene . . . . .	i, 459
TEXEDUR (ERNESTO). Some New Polymerides of the Phenols with Propenyl Side-chains . . . . .	i, 460
TEXEDUR (ERNESTO). Action of Nitrous Acid on Ethylbenzene . . . . .	i, 460
RAVAGELLINI (GUIDO). Some Derivatives of Hydroxyquinol. IX. . . . .	i, 460
TSCHELINCEV (VLADIMIR V.) and B. V. PAVLOV. Behaviour of Individual Organo-magnesium Compounds Towards Aromatic Ethers . . . . .	i, 461
GOESKI (ALEXANDER I.). Reduction by means of Organo-magnesium Compounds . . . . .	i, 462
ROSENTHAL (KARL W.). Phenylethanolamines, Phenylnitroethanols, and their Hydroxy-derivatives . . . . .	i, 462
FISCHL (S.). Action of Sulphuric Acid on Tetramethylammoniumhydroxide. The Pinacol of Michler's Ketone . . . . .	i, 465
ZELINSKI (NICOLAI IL.) and M. N. UERDINOV. 1:1-Dimethylolcyclo- butane . . . . .	i, 466
BEAUFORT (HENRI). The Iodolhydrin of the Glycol Derived from Cinnamyl Methyl Ether . . . . .	i, 466
BEAUFORT (HENRI). Alkylololhydrins Derived from Cinnamyl Methyl Ether . . . . .	i, 467
FAHRNFARBRKEN VOEM, FEIDER, BAYER & Co. Preparation of Aromatic Amino-alcohols . . . . .	i, 467
TSCHECHIRADIN (ALEXEI E.). 1-Methylcyclopentane-1-carboxylic Acid . . . . .	i, 467
HINTIKKA (S. V.). Dihydrocinnophenone Acid (Cinnaphenilic Acid) and the Action of Sodium on Cinnaphenilone . . . . .	i, 468
SABATIER (PAUL) and MARCEL MEYER. Direct Hydrogenation of the Hydrocyanic Esters: Preparation of <i>Benzyldimethylammonium</i> Acid . . . . .	i, 468
HEMMELMAYR (FRANZ VON). Influence of the Nature and Position of Substituents on the Stability of the Carboxyl Group in Substituted Benzoic Acids . . . . .	i, 468
RIEDEL (J. D.). Preparation of Nuclear Nitroso-derivatives of Phenyl- glycine- $\alpha$ -carboxylic Acids, their Acids and Neutral Esters . . . . .	i, 469
GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL. Preparation of Derivatives of Arylalkoxyacetic Acids . . . . .	i, 469
SANDELIN (A. E.). Stereoisomeric <i>iso</i> -Tenchloranaphoric Acids . . . . .	i, 469
CURTIS (THEODORE) and AUGUST SIMPSON. Behaviour of the 1-Ester of 3-Nitrophthalic Acid Towards Hydrazine . . . . .	i, 472
WARK (ANDREW) and M. DOLL. Preparation of $\alpha\alpha$ -Diketonic Esters . . . . .	i, 473
HOESCH (KURT). Synthesis of Oxalic Acid and Fumaric Acid . . . . .	i, 474
WERNER (HEINRICH) and WOLFGANG FELIX VON OEFFINGEN. Hydro- genation of Santonin . . . . .	i, 474
WIEPRAND (EDGAR) and E. BENNETT. Santonin. XI. Tetrahydro- santonin . . . . .	i, 476
BADISCHE ANILIN- & SODA-FABRIK. Preparation of 1-Amécanthra- quinone-2-carboxylic Acids and their Derivatives . . . . .	i, 476
LIEBERMANN (CARL) and M. KAHN. Esters of Polycyanamide Acid . . . . .	i, 476
FISCHER (EMIL) and HERMANN O. L. FISCHER. Methylcarbamate-deriv- atives of Phenolcarboxylic Acids and their Use for Synthetic Operations. VIII. Derivatives of Osellinic and $\alpha$ -Resorcylic [3:5-Dihydroxybenzoic] Acids . . . . .	i, 477
FISCHER (EMIL) and KARL FREUDENBERG. Tannin and the Synthesis of Similar Substances. III. Compounds of High Molecular Weight . . . . .	i, 479
LOCKEMANN (GEORG) and FRANZ LECHS. Substituted phenylhydrazones BIANCHI (I. G.). Condensation Product of Piperonaldehyde with Ethyl Urethane . . . . .	i, 482
FAHRNFARBRKEN VOEM, FEIDER, BAYER & Co. Preparation of Cyclo- ketones . . . . .	i, 482
WALLACH (OTTO) [with LOUIS ADAMSCHER, FR. HENDERS, and RUD. MÜLLER]. Terpenes and Etheral Oils. CXV. . . . .	i, 482



	PAGE
MEERWEIN (HANS) [with F. KREEMERS, HANS PROBST, and R. SPITZGARD]. Pinacolin Transformation. II. Asymmetric Cyclic and Acyclic Pinacones and Their Transformation Products . . . . .	i, 185
HALLER (ALBIN) and EDOUARD BAEHL. Syntheses by means of Sodamide . . . . .	i, 188
WAHL (WALTER A.). A Fourth Modification of Benzophenone . . . . .	i, 188
MEYER (KURT H.) and ALBERT SANDER. Anthracene. III. Derivatives of Anthrone . . . . .	i, 189
SCHIEBER (JOHANNES) and PAUL HEROLD. Experiments on the Determination of the Constitution of Enolic Substances . . . . .	i, 190
SCHIEBER (JOHANNES) [with K. KLOPPE and K. SCHNABEL]. Phthalylglyceryl Derivatives of Acetylacetone, Benzoylacetone, and Ethyl Cyanoacetate . . . . .	i, 191
SEYEWITZ (ALPHONSE). Action of Hydrochloric Acid on <i>p</i> -Benzoquinone-sulphonic Acid . . . . .	i, 192
ISKATI (CONSTANTIN I.) and M. A. MIHAILESCU. Action of Nitrous Acid on Dianilino- <i>p</i> -benzoquinonacril . . . . .	i, 192
MEYER (RICHARD). Metaquinonoids . . . . .	i, 193
FAERENFABRIKEN VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Anthraquinone from Anthracene . . . . .	i, 193
SCHILLING (H.). Preparation of Chlorinated Anthraquinones and Anthracenes . . . . .	i, 194
FAERENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of Selenocyanates of the Anthraquinone Series . . . . .	i, 194
UELMANN-GOLDBERG (ERMA). Preparation of 2-Anthraquinone Sulphide . . . . .	i, 195
HALLER (R.). Action of Colloidal Metallic Hydroxides on Hydroxy-anthraquinones . . . . .	i, 195
FRANCESCOINI (LUIGI) and F. SERNAGIOTTO. Bupleurol or Dihydroneol. Constitution. II. . . . .	i, 195
BLUMANN (ARNOLD) and OTTO ZFITSCHKE. The Autoxidation of Turpentine . . . . .	i, 196
HÄMÄLÄINEN (JUHO). Synthetic $\beta$ -Glucosides of the Terpene Alcohols . . . . .	i, 197
BOURQUELOT (EMILE) and MARC BRIDEL. Synthesis of Alkyl Glucosides by means of Emulsin, $\beta$ -Phenylethyl Glucoside, and $\beta$ -Cinnamyl Glucoside . . . . .	i, 198
BOURQUELOT (EMILE) and MARC BRIDEL. Synthesis of Alkyl Galactosides by means of Emulsin. $\beta$ -Methyl Galactoside and $\beta$ -Allyl Galactoside . . . . .	i, 198
KRASOVSKI (N.). Rhodoxanthin from <i>Rhamnus cathartica</i> and Frangulin from <i>Rhamnus frangula</i> . . . . .	i, 198
FAERENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of the Active Principle of Apocynum . . . . .	i, 198
ZETNEK (RICHARD VON). The Blue Pigment from <i>Cornilabrus pava</i> . . . . .	i, 199
WILLSTÄTTER (RICHARD) and LENSART FORSEN. Chlorophyll. XXI. Introduction of Magnesium into Chlorophyll Derivatives . . . . .	i, 199
PILOTY (OSKAR). [Action of Sodium Methoxide on Bilirubin Acid, Bilirubin, and Hemibilirubin] . . . . .	i, 200
ADLER-HELMARK (JENNY). The Action of Hydrogen Peroxide on Hippocelatin . . . . .	i, 200
FISCHER (EMIL) and FRITZ BRAUNS. Furoylformic Acid and Furoylglycollic Acid . . . . .	i, 201
NIERENSTEIN (MAXIMILIAN). Hydroxycatechin and Catechin-carboxylic Acids . . . . .	i, 201
WEIDLEIN (EDWARD R.). Adrenaline from the Whale . . . . .	i, 202
FREUND (MARTIN). Berberine . . . . .	i, 202
FREUND (MARTIN) and KARL FLEISCHER. Derivatives of Benzyl-dihydroberberine . . . . .	i, 202
FREUND (MARTIN) and HANNS COMMESSMANN. Methyl-dihydroberberine and its Derivatives . . . . .	i, 204
FREUND (MARTIN) and HANNS COMMESSMANN. Ethyl-dihydroberberine and its Derivatives . . . . .	i, 205

	PAGE
FREUND (MARTIN) and ROBERT LACHMANN. <i>iso</i> Propyldihydroberberine and its Derivatives . . . . .	i, 507
FREUND (MARTIN) and HAROLD HAMMEL. <i>iso</i> Butyldihydroberberine and its Derivatives . . . . .	i, 509
FREUND (MARTIN) and DANIEL STEINBERGER. <i>n</i> -Octyldihydroberberine and <i>iso</i> Amyldihydroberberine and Their Derivatives . . . . .	i, 510
FREUND (MARTIN) and EUGEN ZORN. Phenyldihydroberberine and its Derivatives . . . . .	i, 511
CHEMISCHE FABRIK VON FRIEDR. HEYDEN. Preparation of Morphine Esters of Halogenated Fatty Acids . . . . .	i, 512
CORRIGA (LOUIS). The Symmetry of Sparteine . . . . .	i, 512
FRITZ (OSKAR) and JOSEF STUCK. Homopicrole . . . . .	i, 512
FABRICENFABRIKEN VORM. FRIEDR. BAYER & CO. Preparation of a Dichloroisatin [and of 5:7-Dichloroisatin] . . . . .	i, 513
FABRICENFABRIKEN VORM. FRIEDR. BAYER & CO. Preparation of a Dichlorobromoisatin . . . . .	i, 513
RADE (PAUL). Lepidylamine . . . . .	i, 513
RADE (PAUL) and RICHARD PASTERNAK. Quinolyl Ketones. I. . . . .	i, 513
RADE (PAUL) and RICHARD PASTERNAK. Quinolyl Ketones. II. . . . .	i, 514
SCHOLTZ (MAX) and W. FRAUDE. Nature of Picolide and Pyrindole. Action of Propionic Acid on $\alpha$ -Picoline . . . . .	i, 514
LANGE (MARTIN). Preparation of Methylcarbazole . . . . .	i, 515
CASSELLA & CO. (LEOPOLD). Preparation of <i>N</i> -Alkylcarbazolesulphonic Acids . . . . .	i, 516
DECKER (HERMAN) and PAUL BECKER. Ammonium-amides and the Action of Anilines on Cyclammonium Salts and Analogous Compounds . . . . .	i, 517
FABRICWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Anthracene Derivatives Containing Nitrogen . . . . .	i, 518
WALL (ANDRÉ) and P. BAGARD. Syntheses in the Group of the Indoloids . . . . .	i, 519
ANILIN GESELLSCHAFT FÜR ANILINFABRIKATION. [Preparation of 1-Chloro-2-nitro-2:4-diethylphenylenediamine] . . . . .	i, 519
VAUDEL (WILHELM). Existence of Phenylhydride . . . . .	i, 519
FABRICWERKE VORM. MEISTER, LUCIUS & BRÜNING. [Preparation of Anthraquinone Derivatives] . . . . .	i, 519
BAISCHE ANILIN- & SODA-FABRIK. [Preparation of Indigoid Compounds] . . . . .	i, 519
SCHOLTZ (MAX). Action of Aliphatic Ketones on Indole and its Homologues: Polymeric Indoles . . . . .	i, 520
DARATSKY (ARGST). The Constitution of the Pyrazolinocarboxylic Acids. III. . . . .	i, 520
TSARALOTOS (DEMETRIUS E.). Constitution of Hypnol . . . . .	i, 521
GRIFFITHS (MARIO). Some New Derivatives of Picrozine . . . . .	i, 521
JOHNSON (TRENT B.) and ZAI ZIANG ZEE. Pyrimidines. LX. Alkylation with Benzyl Chloride . . . . .	i, 521
KIEHMANN (FRIEDRICH). [Thedazine] Correction . . . . .	i, 522
NOELTING (EMILIO) and J. SAAS. The Triphenylmethane Colour Bases . . . . .	i, 522
MICHAELIS (ARGST) and ARTHUR SCHAFER. 5-Aminopyrazole and Indopyrines. III. 5-Imino-1-phenyl-3-methylpyrazole . . . . .	i, 524
MICHAELIS (ARGST) and LUDWIG KLAPPERT. 5-Amino-1- <i>ortho</i> - and <i>para</i> -tolyl-3-methylpyrazoles . . . . .	i, 525
MICHAELIS (ARGST) and WILHELM TITMUS. 5- <i>ortho</i> -Carboxylic Acids of Anilopyrine and their Esters . . . . .	i, 527
ENGLAND (R.) and FRIEDRICH KITSCHER. Synthesis of Herzynine . . . . .	i, 529
BARGER (GEORGE) and ARTHUR J. EWINS. The Identity of Trimethyl-histidine (Histidine-betaïne) from Various Sources . . . . .	i, 529
WELLSCH (JULIUS). Synthesis of $\alpha$ -Ketoaldehydes from Tyrosine, Tryptophan and Histidine . . . . .	i, 529
MEYER (HANS) and FRIEDRICH SCHAFFEN. Derivatives of <i>iso</i> Cinchomeronic Acid and 2:5-Diaminopyridine . . . . .	i, 530

	PAGE
WAHL (ANDRÉ) and M. DOLL. Preparation of Acylacetic Esters . . . . .	i, 501
CHEMISCHE FABRIK GRIESHEIM-ELCKRON. [Preparation of an Anthracene Derivative]	i, 503
ANGELI (ANGELO) and BRUNO VALORI. New Derivatives of Azoxybenzene .	i, 503
OPPE (ALFRED). Diazo-compounds derived by the Action of Alkali on Nitrosophthalimidine. Simplified Preparation of Nitrosophthalimidine	i, 504
CHARRIER (G.) and G. FERRERI. Etherification of <i>o</i> -Hydroxyazo-compounds. II.	i, 505
MEYER (KURT H.) and KARL ZAHN. Hydroxyazo-compounds and Quinone-phenylhydrazones of the Anthracene Series . . . . .	i, 506
CĂLUGĂREANU (D.). Action of Acids on Proteins . . . . .	i, 508
COOPER (EVELYN A.). The Relations of the Phenols and their Derivatives to Proteins. Mechanism of Disinfection. II. Effects of Various Factors on the Germicidal and Protein-precipitating Powers of the Phenols	i, 508
COOPER (EVELYN A.). The Relations of the Phenols and their Derivatives to Proteins. Mechanism of Disinfection. III. The Chemical Action of <i>p</i> -Benzquinone on Proteins . . . . .	i, 508
KOSSEL (ALBRECHT) and FRANZ WEISS. Nitro-derivatives of the Proteins	i, 509
BONGIOVANNI (CORRADO). Action of Arsenious Acid, Arsenic Acid, and Phosphoric Acid on Albumin . . . . .	i, 509
PILOTY (OSKAR) and EDMUND DORMANN. Acid Decomposition Products of Hæmin . . . . .	i, 509
HAMSKÉ (ANT.). Sulphuric Acid Hæmatoporphyrin . . . . .	i, 510
MICHAELIS (LEONOR) and (Miss) MAUD L. MENTEN. The Kinetics of Invertin Action . . . . .	i, 510
KOPACZEWSKI (LADISLÁS). The Dialysis of Maltase . . . . .	i, 511
PANZER (THEODOR). Action of Ammonia Gas on Diastase. III. . . . .	i, 511
BOUQUELOT (EMILE) and EMILE VERDON. The Reversibility of Ferment Actions: Emulsin and <i>β</i> -Methyl Glucoside . . . . .	i, 512
TEODORESCO (E. C.). Action of High Temperatures on the Dried Nucleases of Vegetable Origin . . . . .	i, 512
FAREWELKE VORM. MEISTER, LEUCUS & BÜCKING. Preparation of a Nitro- <i>β</i> -aminophenyl-1-arsinic Acid . . . . .	i, 512

*Physiological Chemistry.*

BACH (ALEXIS). Oxidising and Reducing Enzymes and their Role in the Process of Respiration . . . . .	i, 513
GASSER (H. S.) and ARTHUR S. LOEVENHART. Mechanism of Stimulation by Lack of Oxygen . . . . .	i, 513
LOEB (ADAM). The Relationship between the Sugar Content of Erythrocytes and Glycolysis . . . . .	i, 513
SCHREIBER (E.) and LÉNÁRD. Oxysterol . . . . .	i, 514
MIVRA (SOICHIRO). The Nature of the Destruction of Hæmoglobin during the Autolysis of Organs . . . . .	i, 514
LEVENE (PHILIPUS A.) and GUSTAV M. MEYER. The Action of Leucocytes on Some Hexoses and Pentoses. III. Mechanism of Lactic Acid Formation from Carbohydrates . . . . .	i, 514
RONA (PETER) and DENGÖ TAKAHASHI. The Behaviour of Calcium in the Serum . . . . .	i, 511
STASSANO (HENRI). Mode of Action of the Anti-coagulating Substance of the Plasma of Propeptone . . . . .	i, 515
SHAW (T. P.). Digestion in the Chick . . . . .	i, 515
DAVIDSON (HEINRICH). The Dependence of Lipase Action on the Concentration of the Hydrogen Ion . . . . .	i, 515
LAQUEUR (ERNST). Method of Investigating Metabolism in Rabbits, Milk being the Only Food . . . . .	i, 516

	PAGE
ISWATERS (HUBERT W.) and A. RENDLE SHORT. Amino-acids and Sugar for Rectal Feeding . . . . .	i, 546
KATER (HENRY S.). The Functions of the Liver in the Metabolism of Fats. I. . . . .	i, 546
ABDERHALDEN (EMIL) and ARNO ED. LAMPE. The Influence of Urea Administered by the Mouth on the Nitrogenous Metabolism of Pigs . . . . .	i, 547
GRAFE (EDUARD). Nitrogen Retention after Feeding on Urea. Reply to Abderhalden and Lampe . . . . .	i, 547
SALANT (WILLIAM) and J. B. RIEGER. Influence of Caffeine on Creatine and Creatinine Metabolism . . . . .	i, 547
HEWITT (JAMES ARTHUR). Metabolism of Nitrogenous Sugar Derivatives . . . . .	i, 547
LAQUEUR (ERNST). The Action of Carbon Dioxide on Metabolism. Autolysis and Metabolism. VI. . . . .	i, 547
ABDERHALDEN (EMIL) and PAUL HIESCH. Synthetic Powers of Animal Cells. The Action of Sodium Nitrate on Nitrogenous Metabolism . . . . .	i, 548
TAYLOR (ALONZO E.) and A. I. RINGER. Utilisation of Ammonia Nitrogen in Protein Metabolism . . . . .	i, 548
GRAFE (EDUARD). Nitrogenous Assimilation on Feeding on Small Amounts of Protein and Large Amounts of Ammonium Salts and Urea . . . . .	i, 548
STICK (HANS). The Location of Protein Synthesis and the Production of Nitrogenous Equilibrium with Minimal Amounts of Proteins of Varying Decomposibilities . . . . .	i, 548
MCCOLLUM (ELMER V.). The Influence of the Plane of the Protein Intake on Nitrogen Retention in the Pig . . . . .	i, 549
MCCOLLUM (ELMER V.) and H. STENROCK. Metabolic End-Products of the Lipoid Nitrogen of Egg-yolk . . . . .	i, 549
BROSA (G. ALESSANDRO). The Biological Value of $\alpha$ -Nucleic Acid . . . . .	i, 549
BORDANDY (STEFAN VON). Resorption of Iodide from the Intestine . . . . .	i, 549
ABDERHALDEN (EMIL), ARNO ED. LAMPE, and EFIM S. LONDON. The Fate of Protein Cleavage Products in the Intestine . . . . .	i, 550
COERT (RUDOLF). The Absorption of Magnesium Sulphate Solutions in the Small Intestine, and the Mode of Action of Saline Purgatives . . . . .	i, 550
WHIPPLE (GEORGE H.). Intestinal Obstruction. A Toxic Substance in the Intestinal Mucosa . . . . .	i, 550
STENROCK (H.) and EDWIN B. HART. The Influence of Function on the Lime Requirements of Animals . . . . .	i, 550
HART (EDWIN B.) and H. STENROCK. The Effect of a High Magnesium Intake on Calcium Retention in Swine . . . . .	i, 550
KNAFFEL-LENZ (ERICH VON) and ERNST P. PICK. The Behaviour of Plastins in the Animal Body . . . . .	i, 551
MCCOLLUM (ELMER V.) and MARGUERITE DAVIS. The Influence of the Composition and Amount of the Mineral Content of the Ration on Growth . . . . .	i, 551
DAVIS (L. H.) and A. D. EMMETT. The Chemical Changes Occurring in Meats during Drying in a Vacuum . . . . .	i, 551
HODDAS (JULIUS). The Presence of Choline or Allied Bases in the Saliva of the Horse . . . . .	i, 551
PIGHINI (GIACOMO), PIETRO BARBIERI, and DOMENICO CARPONE. The Central Nervous System under Normal and Pathological Conditions. V. Biochemical Studies on Brain Swelling: (a) Acute Brain Swelling and the Colloidal Theory of Edema . . . . .	i, 551
GREY (ROBERTON CHARLES). The Fatty Acids of the Human Brain . . . . .	i, 552
MOORHOUSE (V. H. K.). Action of Various Influences on the Mahmalian Heart . . . . .	i, 552
GEOS (OSKAR). The Action of Oxalic Acid on the Frog's Heart . . . . .	i, 552
BANG (IVAR). Diastases. II. Sugar Formation in the Frog's Liver. I. . . . .	i, 552
BANG (IVAR). Diastases. III. Sugar Formation in the Frog's Liver. II. . . . .	i, 553

	PAGE
PARNAS (JAKOB). The Formation of Glycogen from Glyceraldehyde in the Liver . . . . .	i, 551
WACKER (LEONHARD) and WERNER HUECK. The Importance of Cholesterol in the Organism . . . . .	i, 554
KOCH (FRED C.). The Iodine-containing Complex of Thyreo-globulin . . . . .	i, 554
SAKAKI (C.). Some Phosphatides of Human Placenta. I. and II. . . . .	i, 554
KLEFFELD (GEORGES). Muscular Contraction; Influence of Non-electrolytes, Electrolytes, and Osmotic Pressure . . . . .	i, 555
CABELLA (MARIO). Amount of Creatine in Muscles of Various Animals and in Different Types of Muscles . . . . .	i, 556
LEO (H. T.) and PAUL E. HOWE. Muscle-Creatine. Dialysis of Creatine from Dog's Muscle . . . . .	i, 555
SIEBECK (RICHARD). The Action of Potassium Chloride on Frog's Muscle . . . . .	i, 556
BRADLEY (HAROLD C.). Connective Tissues of Limulus . . . . .	i, 556
KACHRISKOWSKI (K.). The Secretion of Pigments by Annelida . . . . .	i, 556
MOORE (BENJAMIN), EDWARD WHITLEY, and ALFRED ADAMS. The Role of Glycogen, Lecithides, and Fats in the Reproductive Organs of Echinoderms . . . . .	i, 556
MOORE (BENJAMIN), EDWARD WHITLEY, and ARTHUR WEBSTER. The Basic and Acidic Proteins of the Sperm of <i>Echinus esculentus</i> . Direct Measurements of the Osmotic Pressure of a Protamine or Histone . . . . .	i, 556
DEZEWINA, (Mme.) ANNA and GEORGES ROHN. Anoxybiore and Chemical Polarity . . . . .	i, 557
CZYHLARZ (ERNEST VON), ADOLF FUCHS, and OTTO VON FÜRTH. The Composition of Human Bile . . . . .	i, 557
LAUNOY (L.) and KARL OCHSLEIN. Secretin and Vaso-dilatin . . . . .	i, 557
FUNK (CASIMIR). An Attempt to Estimate the Vitamine-fraction in Milk . . . . .	i, 557
LÉFINE (RAPHAEL) and RAYMOND BOLLER. The Secretion of the Two Kidneys . . . . .	i, 558
HENDERSON (LAWRENCE J.) and WALTER W. PALMER. The Extremes of Variation of the Concentration of Hydrogen Ions in Human Urine . . . . .	i, 558
MAYER (ERNST). Diastase in the Urine of Infants . . . . .	i, 558
GIVENS (MAURICE H.) and ANDREW HUNTER. Excretion of Purine Katabolites in Sundry Types of Mammalia . . . . .	i, 558
CORBETT (DUDLEY). Estimation of Amyolytic Ferments in the Urine as a Measure of Certain Pathological Conditions . . . . .	i, 558
WOODYATT (R. T.). Sarcosolactic Acid and the Theory of Diabetes . . . . .	i, 559
ROLLY (FR.) and FR. OPPERMANN. The Behaviour of Blood Sugar in Normal and Pathological Cases. VII. The Blood Sugar in Diabetes Mellitus . . . . .	i, 559
STADTMÜLLER (N.), MAX KARS, and JACOB ROSENBLUM. Sulphur Metabolism. I. The Urinary Sulphur Partition in Various Diseases . . . . .	i, 559
BERTHELOT (ALBERT) and D. M. BERFRAND. The Intestinal Flora. The Possible Production of Ptomaines in Acid Medium . . . . .	i, 560
BERRAR (M.). The Action of Aloin on Metabolism. The Physiology of Artificially Produced Gout and Fever . . . . .	i, 560
DUNN (JOHN SHAW). Use of the Oxydase Reaction in the Differentiation of Acute Leucemias . . . . .	i, 560
KISCH (BRUNO). Narcosis . . . . .	i, 561
SCHREYER (SAMUEL B.) and CHARLES SINGER. Gastric Juice in Malignant and Non-malignant Diseases of the Stomach and Duodenum . . . . .	i, 561
WELLS (H. GIBSON) and O. F. HEDENBERG. The Entrance of Iodine into Diseased Tissues . . . . .	i, 562

# CONTENTS.

x1

	PAGE
MENEZUZZI (RODOLFO). Pharmacological Investigations of Ammonium Chloride . . . . .	i, 562
SALOWSKI (ERNST). Behaviour of Mercury [in the Organism] . . . . .	i, 562
DOMINICI (HENRI), (Mme.) SIMONE LABORDE, and ALBERT LABORDE. The Injection of Salts of Iodine . . . . .	i, 562
PLESCH (J.), LASZLO KARCZAG, and BRUNO KERTMAN. Thorium-X in Biology and Pathology . . . . .	i, 563
MAASS (THEODOR A.) and J. PLESCH. Action of Thorium-X on the Circulation . . . . .	i, 563
PAPPENHEIM (A.) and J. PLESCH. Experimental and Histological Investigation of the Action of Thorium-X on the Animal Organism . . . . .	i, 563
DRESER (HEINRICH). Pharmacological Differences between <i>cis</i> - and <i>trans</i> -Isomerides . . . . .	i, 563
MAYER (PAUL). Pyruvic Acid Glycosuria. II. The Question of Sugar Formation from Pyruvic Acid . . . . .	i, 561
MURA (SOICHIRO). The Action of Methyl Alcohol on the Circulating Blood . . . . .	i, 564
STENSTRÖM (THOR). Caffeine Hyperglycemia . . . . .	i, 564
PIGORINI (LUCIANO). The Behaviour of Dextrose-Resorcinol in the Animal Organism . . . . .	i, 564
NITREBO (CARL). The Destruction of $\alpha$ -Hydroxypropaldehyde and Methylglyoxal by Animal Organs . . . . .	i, 564
SALOWSKI (ERNST). The Behaviour of Ferric Iodopiraniculate in the Organism . . . . .	i, 565
JAKIN (HENRY D.) and HAROLD W. DUDLEY. Enzyme Concerned with the Formation of Hydroxy-acids from Ketonic Aldehydes . . . . .	i, 565
SWEET (JOSHUA E.) and A. I. RINGER. The Influence of Phloridzin on Dogs with Eck's Fistula . . . . .	i, 565
AUSTIN (JOSHUA H.) and A. I. RINGER. The Influence of Phloridzin on a Splenectomised Dog . . . . .	i, 566
RIVA (ANTONIO). Lead Compounds in the Organism . . . . .	i, 566
SELLEI (JOSEF). The Action of Dyes in Conjunction with Poisons and Medicaments . . . . .	i, 566
BERESIN (W. I.). Influence of Poisons on the Isolated Heart of the Fish . . . . .	i, 566

## Chemistry of Vegetable Physiology and Agriculture.

GOUFFÉ (R.). The Phosphorus Compounds formed by <i>Antylophora bonari</i> . . . . .	i, 567
DREW (G. HATOLD). The Precipitation of Calcium Carbonate in the Sea by Marine Bacteria . . . . .	i, 567
MAZE (PIERRE). Alcoholic Fermentation of Lactic Acid . . . . .	i, 567
HASTINGS (E. G.) and EDWIN B. HAFT. An Acid-producing Enzyme in <i>Bacterium lactis acidi</i> . . . . .	i, 567
KOS-SOWICZ (ALEXANDER) [with L. VON GÖLLE]. Employment of Lactic Acid and Lactic Acid Bacteria in the Pickling of Cucumbers . . . . .	i, 568
AMBRÖZ (ADOLF). A New Thermophilic Bacterium . . . . .	i, 568
LEMELEY (ALEXANDER VON). The Mechanism of Alcoholic Fermentation . . . . .	i, 568
SLATOR (ARTHUR). The Rate of Fermentation by Growing Yeast Cells . . . . .	i, 568
ELEF (HANS VON) and DAVID JOHANSSON. Chemical Composition and Formation of Enzymes. VIII. Simultaneous Variation in Amount of Invertase and Fermenting Enzyme in Living Yeast . . . . .	i, 568
HARPER (ARTHUR). The Enzymes of Washed Zymoin and Dried Yeast (dehobey). I. Carboxylase . . . . .	i, 568

	Page
BOKORNY (THOMAS). Action of Free Ammonia on Yeast. Comparison with Other Bases	i, 549
BOKORNY (THOMAS). Microchemical Detection of Potassium in Yeast and Other Cells	i, 549
BOKORNY (THOMAS). Action of Certain Metallic Salts on the Development of Yeast and the Germination of Barley	i, 549
BOKORNY (THOMAS). Action of Uranium, Molybdenum, and Vanadium Salts on Yeast and Other Micro-organisms	i, 549
BOKORNY (THOMAS). Influence of Different Substances on the Germination of Vegetable Seeds. I, II, and III.	i, 549
VARVARO (UGO). Action of Manganese Dioxide and of Other Metallic Compounds on the Germination of Seeds	i, 579
BERNARDINI (LUIGI) and F. GALLUCCIO. Formation of Pentosans in the Germination of Seeds	i, 579
PALLADIN (VLADIMIR L.). Respiration of Plants as Hydrolytic Oxidation	i, 579
BOBOVIKOV (G. A.). Causes of Growth of Plants	i, 571
DECKER (HERMANN). Formaldehyde and Plant Syntheses	i, 571
OSTERHOUT (WINTHROP J. V.). Plants which Require Sodium	i, 571
BOKORNY (THOMAS). Antagonistic Action of Chemical Substances on Fungi. Chemical Preservation	i, 571
KOSSOWICZ (ALEXANDER). Assimilation of Nitrates by Moulds	i, 571
KOSSOWICZ (ALEXANDER). Decomposition of Carbamide, Uric Acid, Hippuric Acid, and Glycine by Moulds. II.	i, 572
ZELLSNER (JULIUS). Chemistry of the Higher Fungi. IX. Galls Produced by <i>Enbasidium Faeinif.</i> Woron., on <i>Rhododendron ferrugineum</i> , L.	i, 572
ZELLSNER (JULIUS). Chemistry of the Higher Fungi. X.	i, 572
MAISONI (GIULIO). Extraction of the Colouring Matter from the Cherry and Investigations of its Properties	i, 574
POWER (FREDERICK B.) and HENRY BROWNING, jun. Chemical Examination of <i>Euphorbia pulchifera</i>	i, 574
WHITBY (G. STAYFORD). Causes of the Natural Changes in the Latex of <i>Hevea Brasiliensis</i>	i, 575
ARMSTRONG (HENRY E.), E. FRANKLAND ARMSTRONG, and EDWARD HORTON. Herbage Studies. II. Variation in <i>Lotus Corniculatus</i> and <i>Trifolium repens</i> (Cyanophoric Plants)	i, 575
IEELE (JOSEF). Chemistry of Peat Moss (Sphagnum)	i, 575
GORTS (A.), M. MARCÉ, and CH. VISCHNAC. Glucosides and Oils of the Primrose	i, 576
POYARNIN (GEORGEI GEORGEVITSCH) and A. BARABANOV. Willow Bark. I.	i, 576
POYARNIN (GEORGEI G.) and N. SHCHAVLEY. Willow Bark. II.	i, 576
HANSEN (ADOLPH). Mannring of Cultivated Plants by means of Carbon Dioxide	i, 577
BLANCE (EDWIN). Importance of the Potassium in Felspar for Plants	i, 577
VILMORIN (Ph. DE) and FERDINAND LEVALLOIS. History of Maize Sugar.	i, 577
ZENTZ (NATHAN), RICHARD VON DER HEIDE, KLEIN, I. VON MARKOFF, FERST VON DESCHANDIER, and QUADKOW. Respiration and Metabolism in Ruminants	i, 577
KÜNG (JOSEF), JULIUS HASENBÄUMER, and K. GLENK. Employment of Dialysis in the Estimation of the Oxidising Power of Soils	i, 577
GRIGNOZ (K. K.). Colloidal Substances in Soil Solutions. Production of Soda in Soils. Alkali and Salt Soils	i, 577
DEMOLIS (A.). The Fertilising Action of Sulphur	i, 579
SCHNEIDERWIND (W.). [Manual] Action of Different Forms of Nitrogen	i, 579
MISCHKELEICH (EILHARD A.) and W. SUMMERMACHER. Influence of Ammonium Sulphate on the Phosphate Mannring of Oats	i, 580
SCHULZE (BERNHARD). Mannring with Sodium Salts	i, 580
IMMENDORFF (HEINRICH). Lime Rich in Silica as Manure	i, 580

## PART II.

*General and Physical Chemistry.*

	PAGE
AUREL (EDMOND VAN). Refractive Index of Substances at their Critical Temperatures . . . . .	ii, 357
CUTHBERTSON (CLIVE). Refraction and Dispersion of Gaseous Compounds and the Cause of the Divergence from Additive Relations . . . . .	ii, 357
CUTHBERTSON (CLIVE) and (Mrs.) MAUDE CUTHBERTSON. Refraction and Dispersion of the Halogens, Halogen Acids, Ozone, Steam, Oxides of Nitrogen and Ammonia . . . . .	ii, 358
BODROUX (FERNAND). Some Liquid Mixtures Specially Suitable for the Observation of Christiansen's Phenomenon . . . . .	ii, 358
ZEYNEK (RICHARD VON). A Modified Hüfner Spectrophotometer . . . . .	ii, 359
BECKMANN (ERNST) and H. LINDNER. Coloured Bunsen Flames . . . . .	ii, 359
WIESER (HEINRICH). Doppler Effect of the Series Lines of Oxygen . . . . .	ii, 359
SMITH (HAROLD). Spectroscopic Study of the Electric Brush Discharge in Water and Salt Solutions . . . . .	ii, 360
STARK (JOHANNES), A. FISCHER, and H. KIRSCHBAUM. The Spectrum of the Univalent and of the Bivalent Helium Ion in the Canal Rays . . . . .	ii, 360
BRISSON (HENRI) and CHARLES FARRY. The Wave-lengths of the Rays of Krypton . . . . .	ii, 361
NACKEN (ANDREAS). Measurements in the Magnesium Spectrum with Reference to the International Normals . . . . .	ii, 361
PASCHEN (FRIEDRICH). Systems of Series [Lines] in the Spectra of Zinc, Cadmium, and Mercury . . . . .	ii, 361
LA ROSA (MICHELE). Spectral Investigation of the Arc Light between Carbons at Low Pressures . . . . .	ii, 361
GEY (J. SAM), E. J. SCHAEFFER, and HARRY C. JONES. The Absorption of Light by Water Changed by the Presence of Strongly Hydrated Salts, as Shown by the Radiometer. New Evidence for the Solvate Theory of Solution . . . . .	ii, 362
FARRY (CHARLES) and HENRI BRISSON. The Absorption of the Ultra-violet by Ozone, and the Extremity of the Solar Spectrum . . . . .	ii, 362
BIELECKI (JEAN) and VICTOR HENRI. Absorption of the Ultra-violet Rays by Acetone . . . . .	ii, 363
FRY (HARRY S.). Applications of the Electron Conception of Positive and Negative Valencies. V. Absorption Spectra and Dynamic Formulae of Chloro-, Bromo-, and Iodo-benzene . . . . .	ii, 363
STARK (JOHANNES), WALTER STEUBING, CORNELIS J. ENKLAAR, and PETER LIFF. Ultra-violet Absorption Bands of the Reciprocal Linking of Carbon Atoms . . . . .	ii, 363
STARK (JOHANNES) and PETER LIFF. Ultra-violet Absorption Bands of the Reciprocal Linking of Carbon Atoms. II. Acetylene Linking . . . . .	ii, 365
STARK (JOHANNES) and P. LEVY. Ultra-violet Absorption Bands of the Reciprocal Linking of Carbon Atoms. III. Benzene Linking . . . . .	ii, 365
WEIMER (GEORG). Absorption of Ethylbenzene in the Ultra-violet . . . . .	ii, 367
VALINCHKO (NICOLAI A.). Absorption Spectra and Constitution of Benzene Derivatives. III. Phenols and Methoxy-, Aldehyde- and Nitro-phenols in Alkaline Solutions . . . . .	ii, 367
LONGOBARDI (ERNESTO). Colour and Optical Activity . . . . .	ii, 369
WALKER (E. E.). Processes Operative in Solutions. XXVI. Disturbance of the Equilibrium in Solutions of L-xylose by Salts and by Non-Electrolytes . . . . .	ii, 368
CHARDIER (J.). Magnetic Rotatory Polarisation of Liquid Nitrogen and Oxygen . . . . .	ii, 368



	PAGE
HENRI (VICTOR) and RENÉ WLEMSER. Energy Absorbed in Photochemical Reactions	ii, 568
BRETHELOT (DANIEL) and HENRY GAUDECHON. The Dissociation of Gaseous Compounds by Light; Gaseous Hydrogen Compounds of the Chlorine and Oxygen Groups	ii, 569
VINCENT (J. HERBERT) and J. MARLEY. The Production of Light by Chemical Action	ii, 569
GANASSINI (DOMENICO). Decomposition of Lactic Acid under the Influence of Sunlight	ii, 579
WEIGERT (FRITZ) and LUDWIG KUMMERER. Quantitative Investigation of the Photochemical Transformation of <i>o</i> -Nitrosobenzaldehyde into <i>o</i> -Nitrosobenzoic Acid	ii, 576
SCHILOV (NIKOLAI) and S. FEDOROV. Physico-chemical Studies on Photographic Developers. (Correction)	ii, 571
BIANU (B.). The Secondary Radiation Produced by $\alpha$ -Rays	ii, 571
GEIGER (HANS) and ERNEST MARSDEN. Laws of Deflection of $\alpha$ -Particles through Large Angles	ii, 571
SIEVEKING (HERM.) and L. LAUTENSCHLAGER. Helium in Thermal Springs and Earth Gases	ii, 572
CHADWICK (JAMES) and ALEXANDER S. RUSSELL. Excitation of $\gamma$ -Rays by the $\alpha$ -Rays of Iodine and Radiothorium	ii, 572
BRAGG (WILLIAM H.). Production of Fluorescent Röntgen Radiation	ii, 575
PROUMEN (HENRI JACQUES). Ionisation Accompanying Flame Gases	ii, 575
POHL (ROBERT) and P. PRINGSHEIM. Photo-electric Emission of Electrons by Calcium	ii, 574
BUTAVAND (F.). The Mechanism of Disintegration of Radioactive Substances	ii, 574
MERCK (EMANUEL) and WILHELM EICHHOLZ. Preparation of Solid Therapeutically Active Compounds of Radium	ii, 574
HEIMANN (BEITA) and WILHELM MARCKWALD. The Radium Content of Pitchblendes	ii, 574
METZNER (WALTHER). Chemical Properties of Thorium-C and Thorium-D	ii, 575
FALTA (WILHELM) and L. ZEHNER. Chemical Action of Thorium-X on Organic Substances, Especially on Uric Acid	ii, 576
MUÑOZ DEL CASTILLO (JOSE). Apparatus for Study of the Activity of the Air of the Sub-soil	ii, 576
MUÑOZ DEL CASTILLO (JOSE) and JOSE BARRIO Y FERNÁNDEZ. Activity of the Air of the Sub-soil in October, 1912	ii, 576
MUÑOZ DEL CASTILLO (JOSE) and JOSE BARRIO Y FERNÁNDEZ. Analytical Observation on the Activity of Rain Water	ii, 576
HEVESY (GREGOR VON). The Electronegative Series of the Radioactive Elements. I.	ii, 579
GRÜNNIGEN (EDUARD). Influence of Temperature and Pressure on the Electrical Resistance of Metals	ii, 577
POHL (ROBERT) and P. PRINGSHEIM. The Selective Photo-electric Effect in Reference to Absorbed Light Energy	ii, 577
PLOTNIKOV (VLADIMIR A.) and V. E. KOROTJAN. Electrical Conductivity of Bromine Solutions of Iodine	ii, 575
TUCKER (WILLIAM SANSONE). Electrical Conductivity and Fluidity of Strong Solutions	ii, 575
MICHAELIS (LEONOR) and PETER ROSA. The Dissociation Constants of Certain Very Weak Acids, Especially the Carbohydrates, Measured by Electrometric Methods	ii, 577
HASSELBAUGH (KARL A.). An Improved Method for the Electrometrical Measurement of the Reaction of Biological Liquids	ii, 579
PRING (JOHN N.). The Conditions which Determine the Cathodic Over-voltage	ii, 584
CADY (WALTER G.). Phenomena at the Anode in Discharge Through Gases	ii, 585
FRYCZ (KASIMIR) and STANISLAS TOLLOZKO. Transport Numbers in Antimony Trichloride as Solvent	ii, 586

	PAGE
FENTES (Mlle. E.). The Magnetic Properties of Some Solid Hydrates of Copper and Chromium	ii, 381
WYROUBOFF (GRÉGOIRE). The Magnetism of Anhydrous and Hydrated Salts	ii, 381
HONDA (KÔFARÔ) and HIROMU TAKAGI. [Magnetic] Susceptibility of Iron Steel, Nickel, and Cobalt at Higher Temperatures	ii, 381
AMAGAT (EMILE H.). Saturation Curves and the Law of the Corresponding States	ii, 382
GAY (L.). Adiabatic Expansion in Liquids	ii, 382
MISCLEAUV (CH.). Method for Determining the Latent Heat of Evaporation of Metals	ii, 382
SEGUEN (SAMUEL). A Relation between the Boiling Points and Molecular Weights of the Members of Homologous Series	ii, 382
KRÖNER (A.). Vapour Pressures of the Alkali Metals	ii, 383
HOUSFIELD (WILLIAM R.). Ionic Size in Relation to Molecular Physics, Together with a New Law Relating to the Heats of Formation of Solid, Liquid, and Ionic Molecules	ii, 383
BOHR (WALTER A.) and H. WALLASCH. Heats of Combustion and Transformation of Some Elements. I. Diamond and Graphite	ii, 384
MAUTHEN (A.). Calorimetric Study of the Iron-Carbon System	ii, 385
ZEDOV (PAVEL V.). Heats of Combustion of Cyclic Compounds. II.	ii, 385
GAY (L.) and F. DUCELLIER. The Chemical Interpretation of Special Points on Curves	ii, 387
IRBY (MAURICE). A Simple Method for Determining the Density of Mineral Powders	ii, 387
CHAPIN (HAROLD CANNING). A Modified Victor Meyer Apparatus	ii, 387
GAY (L.). The Expansion Pressure of Normal Fluids	ii, 388
DEBRISAY (RNE). A New Physico-chemical Volumetric Method	ii, 388
PIWNIKIEWICZ (H.). A Simple Apparatus for the Absolute Measurement of the Coefficient of Viscosity of Gases and for the Demonstration of Maxwell's Law	ii, 388
KERNAKOV (NICOLAI S.) and N. N. FEREMOV. Viscosities of the Systems: Chloral-Water and Chloral-Ethyl Alcohol	ii, 388
MOLES (ENRIQUE), M. MARQUINA, and G. SANTOS. Viscosity and Conductivity of Concentrated Solutions of Ferric Chloride	ii, 390
ERDMANN (C. C.). Method for Determining the Surface Tension of Liquids for Biological Purposes	ii, 390
MAKENSINE (N. A.). Influence of Light on the Surface Tension of Various Solutions	ii, 390
HESERUS (NICOLAI A.). Independence of the Surface Tension of Light-sensitive Solutions on the Illumination	ii, 390
ARMSTRONG (HENRY E.) and J. VARGAS EYRE. Processes Operative in Solutions. XXV. Influence of Non-Electrolytes on Solubility. Nature of the Processes of Dissolution and Precipitation	ii, 391
KENNETZOV (PETR). Estimation of the Solubility of Solids in Liquids	ii, 391
BROSTALIER (STIEFRIED). The Formulation and Genetics of the Formation of Solid Solutions in the Dissociation of Oxides	ii, 391
GUTIERA (EMILE). Experimental Investigation into the Physical Conditions for the Crystallisation of Metals	ii, 392
PARRAVANO (NICOLA). Phenomena of Crystallisation in Ternary Systems. VI. Cases with a Gap of Miscibility in the Liquid and also in the Solid State	ii, 392
ISAC (Miss FLORENCE). Spontaneous Crystallisation and the Melting- and Freezing-point Curves of Two Substances which Form Mixed Crystals and the Freezing-point Curve of which Exhibits a Transition Point. Mixtures of <i>p</i> -Bromonitrobenzene and <i>p</i> -Chloronitrobenzene	ii, 392
FEREROV (ENGEAF N.). The First Results of the Study of the Tables for Crystallisation Analysis	ii, 393
SMIS (ANDREAS). A New Theory of the Phenomenon of Allotropy	ii, 393

	PAGE
PIERONI (A.) [with E. TONNIOLI]. New Method for the Preparation of Colloidal Solutions . . . . .	ii, 387
RUHLAND (WILLY). Colloido-Chemical Studies of Protoplasm . . . . .	ii, 383
WEIMANN (PETE P. VON). A Fundamental Law of Dispersoidology . . . . .	ii, 384
REICHARD (C.). Regularities in the Hygroscopy of Chemical Compounds . . . . .	ii, 384
HOFNEN (PETRUS H. J.). Thermodynamic Functions of Mixtures with Reacting Components . . . . .	ii, 394
GRASSI (UGO). Chemical Equilibria in Gaseous Systems . . . . .	ii, 395
BRINER (EMIL). Chemical Reactions in Strongly Compressed Gases . . . . .	ii, 395
MATIGNON (CAMILLE). Chemical Equilibrium in the Action of Hydrogen Chloride Gas on Zinc Sulphate . . . . .	ii, 395
THIEL (ALFRED). Landolt's Reaction as an Example for the Demonstration of the Foundations of Chemical Kinetics . . . . .	ii, 395
THIEL (ALFRED). The Nature of the Time Reaction between Carbonic Acid and Bases . . . . .	ii, 396
FINDLAY (ALEXANDER). Velocity of Formation of Precipitates . . . . .	ii, 397
KILPI (SULO). Hydrolysis and Alcoholysis of Amides . . . . .	ii, 397
PINNOW (JOHANNES). The Simultaneous Oxidation of Quinol and [Sodium] Sulphite by means of Atmospheric Oxygen . . . . .	ii, 398
STIEGLITZ (JULIUS) and GEORGE O. CURME, jun. The Transformation of Hydrobenzene into Azobenzene and Aniline: A Reaction of the First Order . . . . .	ii, 398
BONE (WILLIAM A.). Surface Combustion . . . . .	ii, 398
FORIN (SERGIUS). Catalytic Oxidation at High Temperatures . . . . .	ii, 399
AERL (EMIL) and G. BAUM. Catalytic Studies. III. Catalytic Deviation of a Reaction . . . . .	ii, 399
PESCHKE (ERNST). A Condenser in One Piece for the Kjeldahl Estimation of Nitrogen . . . . .	ii, 400

### *Inorganic Chemistry.*

SFERRE (JOACHIM). The Acidity of Water and of Hydrogen Peroxide and the Uniformity of Compounds. Preliminary Note . . . . .	ii, 400
KUSNETZOV (PETR). Application of Hot Centrifugation to the Estimation of the Composition of Hydrates with Low Water Content . . . . .	ii, 400
JAQUEROD (ADRIEN) and MELCON TOURFALAN. Weight of a Normal Litre of Gaseous Chlorine and Silicon Tetrafluoride. Determination of the Atomic Weights of Chlorine and Fluorine . . . . .	ii, 401
MATHERS (FRANK C.). Preparation of Perchloric Acid . . . . .	ii, 401
FRESENIUS (HEINRICH). The Finding of Iodine in the Waters of the Dead Sea, and the Detection of Iodine in Concentrated Solutions Rich in Magnesium Salts . . . . .	ii, 401
BECKMANN (ERNST) and RUDOLF HANSLIAN. Behaviour of Iodine towards Sulphur, Selenium, and Tellurium . . . . .	ii, 402
FRATS AYMORICH (JOSE). Analysis and Preparation of Fuming Sulphuric Acid of Given Strength . . . . .	ii, 402
GLAUSER (R. TH.). Selenium Oxybromide . . . . .	ii, 403
KUSNETZOV (PETR). The Atomic Weight of Tellurium . . . . .	ii, 403
RUSS (FRANZ). The Oxidation of Nitrogen and Active Nitrogen . . . . .	ii, 403
MANCROT (WILHELM). The Action of Ozone on Liquid Ammonia . . . . .	ii, 403
BILTZ (WILHELM). Tension of Metal Ammine Compounds . . . . .	ii, 404
WARL (WALTER A.). The Allotropy of Phosphorus . . . . .	ii, 404
LÖWENHARDT (E.). Formation of Hydrogen Phosphide from Phosphorus and Potassium Hydroxide . . . . .	ii, 404
SANVER (CHARLES R.) and EMILE R. RIEGEL. The Action of Sulphur Trioxide on Silicon Tetrachloride . . . . .	ii, 405
PECHER (HENRI). The Alteration which takes place in Potassium Polysulphide . . . . .	ii, 405

	PAGE
RENGADE (ÉTIENNE) and N. CONTRAND. The Aohydrone Protosulphides of the Alkali Metals . . . . .	ii, 405
D'ANS (JOHANNES). Acid Sulphates. VII. Acid Sulphates and Pyrosulphates of Sodium, Potassium, and Ammonium . . . . .	ii, 405
DUPFLOU (ALEXIS). A New Form of Potassium Dichromate . . . . .	ii, 406
VESTERBERG (ALBERT). Sodium Silicate. Preparation and Recrystallisation of Sodium Silicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ . . . . .	ii, 406
SELYANOV (FEDOR FEODOROVITSCHEV). Hydrates of Calcium Oxide and their Molecular Compounds. II. Supersaturated Solutions of Hydrated Calcium Oxide . . . . .	ii, 406
SELYANOV (FEDOR F.). Hydrates of Calcium Oxide and their Molecular Compounds. III. Crystalline Hydrates . . . . .	ii, 407
NIELSEN (OTTO). The System Lime, Phosphoric Oxide and Silica . . . . .	ii, 407
MEYER (FRIEDRICH). The Permeability of Glass for Water under the Influence of Electricity of High Tension . . . . .	ii, 408
EGER (GEORG). Ternary Alloys of Magnesium, Aluminium, and Zinc . . . . .	ii, 408
MAZZOTTO (DOMENICO). Influence of Thermal Treatment on the Solidification and Transformation of Cadmium-Tin Alloys . . . . .	ii, 408
BRAND (HELMANN). Crystallisation in the Ternary System Cadmium-Potassium-Sodium Bromides . . . . .	ii, 409
BAKER (MATTHEW). Compounds of Cerium Chloride with Ammonia . . . . .	ii, 409
POZZI-ESPOFF (M. ENMANDELL). A New Double Sulphate of Cerium and Silver . . . . .	ii, 409
SCALA (ALBERTO). Solubility in Water of Lead as a Couple with and as an Alloy with Other Metals . . . . .	ii, 409
DEMASSEIX (Mme. N.). The Equilibrium between Lead Chloride and Ammonium Chloride in Aqueous Solution . . . . .	ii, 409
BROWN (OLIVER W.) and A. E. NEES. Variations of the Physical and Chemical Properties of Red Lead . . . . .	ii, 410
KERN, ROY (NIKOLAI S.), SERGEI F. SHEMITSCHENKO, and V. TAVARIN. Compound of Varying Composition in Alloys of Thallium and Bismuth . . . . .	ii, 410
SCHLEICHER (ALADAE). The Ternary System Copper-Cadmium-Antimony . . . . .	ii, 411
DREIFUS (MARCELL). The Changes in Dilute Mercuric Chloride Solutions . . . . .	ii, 411
ROHLAND (PAUL). The Action of Hydroxyl Ions on Colloidal Clay . . . . .	ii, 412
KISSNER (A.). The Formation of Temper-Carbon in Malleable Castings . . . . .	ii, 412
HANSEN (H.). The Theory of Undercooled Solid Solutions and the Nature of Austenite and Martensite . . . . .	ii, 412
CHILLO (GINO). Formation of Iron Rust . . . . .	ii, 413
LOEBBECH (ERIK) and FRITZ SPITZER. Formation of Rust under Protecting Paint (Coatings) . . . . .	ii, 413
ALTMANN (PAUL). Ethyl Iodides . . . . .	ii, 413
FORBAND (ROBERT DE). Dehydration and Decomposition of the Hydrates of Ureyl Nitrate. Formation of a Monohydrate . . . . .	ii, 413
WEDERKIND (EDGAR), C. HOEST and O. JOCHIM. Synthesis of Berberis in the Electric Vacuum Oven . . . . .	ii, 414
SCHREIBER (WALTER R.). Chinese Antimony Ores, Crude and Regulus . . . . .	ii, 415
PAPAYANOS (NICOLA). The System Antimony-Selenium . . . . .	ii, 415
PAPAYANOS (NICOLA). The System Bismuth-Selenium . . . . .	ii, 415
QUARATOLI (ALFREDO). Hydrolysis of Bismuth Nitrate . . . . .	ii, 416
RIFE (OTTO), F. KISSER and WILLI JEDOU. The Fluorides of the Noble Metals . . . . .	ii, 416
RIFE (OTTO) and FRIEDRICH WILHELM TSCHIECH. Osmium Chlorides . . . . .	ii, 416

### Mineralogical Chemistry.

HILLEBRAND (WILLIAM F.). A Danger to be Guarded Against in Mining Mineral Separations by means of Heavy Solutions . . . . .	ii, 418
PIETRI (ARNALDO). Helium in Chemical Minerals . . . . .	ii, 419

	PAGE
ZAMBONINI (FERRUCCIO). Natural Thio-salts. 1. The Plagionite Group	ii, 419
DOELTER (CORNELIUS) and EMIL DITTLER. Baunite or Sporogelite?	ii, 419
ROGERS (AUSTIN F.), and G. P. BOHART. Delafossite, a Cuprous Meta- ferrite from Bisbee, Arizona	ii, 419
JOVITSCHITSCH (MILORAD Z.). Chromitite	ii, 429
VENDL (ALADÁR). Titaniferous Magnetite in the Basalt of Kresztévány, Hungary	ii, 429
HILLEBRAND (WILLIAM F.) and HERBERT E. MERWIN. Two Varieties of Calciovelberthite (?) from Utah	ii, 429
ORLOV (NIKOLAI A.). Datolite from Mt. Mashuk, Caucasus	ii, 421
TSCHIRVINSEI (PETR N.). [Datolite]	ii, 421
TSCHEERNIK (GEORGI PROKOFEVITSCH). Chemical Examination of Certain Minerals from Ceylon Gravel	ii, 421
HAWKINS (ALFRED C.). Mineral Occurrences at Princeton, New Jersey	ii, 421
FRIEDL (GEORGES). Synthesis of Polassium-Nephelite	ii, 422
KLEMM (G.). Viridine, a Variety of Andalusite	ii, 422
SILBERMÜNTZ (W.). Minerals from the Umen Mtns., Urals	ii, 422
KILLIG (FR.). Alteration of Phyllite into a Compact Paragonite-rock	ii, 423
PIÑA DE RUBIES (SANTIAGO). Composition of Volcanic Magmas	ii, 421
MERRILL (GEORGE P.). Meteoric Iron from Perryville, Missouri	ii, 421

### Analytical Chemistry.

DENNIS (LOUIS M.). A New Form of Orsat Apparatus	ii, 421
RITTOH (O.). A New Dropping Apparatus for Use in Analyses	ii, 421
DONAU (JULIUS). The Quantitative Handling of Small Quantities of Precipitates	ii, 421
THIEL (ALFRED). Application of New Results of the Investigation of Indicators to Quantitative Studies	ii, 422
FLOPENTIN (DANIEL). Ferrous Sulphate Monohydrate and its Use in Volumetric Analysis	ii, 422
CAMPO Y CERRÁN (ANGEL DEL). New Colour Reactions of Hydrogen	ii, 422
MICHEL (FRANZ). Direct Estimation of Water in Food-stuffs and Other Articles by Distillation	ii, 422
LARSSON (K. O.). The Estimation of Chlorine in Urine and Blood	ii, 422
BOGDANDY (STEFAN VON). Estimation of Chloride and Bromide in Organic Fluids	ii, 422
NICOLA (FRANCESCO). Ghraceschi's New Bromine Reaction for the Detection of Bromate in Potassium Chlorate	ii, 422
FRESENIUS (HEINRICH). Detection of Iodine in Concentrated Solutions Rich in Magnesium Salts	ii, 422
COMA Y ROCA (F.). Detection and Estimation of Fluorine in Wines	ii, 422
WALKER (W. H.) and WALTER A. PATRICK. Estimation of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace	ii, 422
CAVEL (LUCIEN). Sulphur and its Variations in the Biological Treatment of Sewage Water	ii, 422
BOSSHARD (EMIL) and W. GEOR. Assay of Hyposulphites	ii, 422
FINCH (GEORGE). The Quantitative Estimation of Sulphuric, Nitric, and Nitrous Acids in Mixed and Waste Acids	ii, 422
SY (ALBERT P.). Apparatus for Fumeless Kjeldahl Nitrogen Digestion	ii, 422
LOMBARD (MATRICE). Estimation of Nitrites in Potable Water	ii, 422
ARTMANN (PAUL) and J. PREISINGER. Estimation of Phosphorus in Iron and Steel	ii, 422
DENNIS (LOUIS M.) and W. J. O'BRIEN. Estimation of Phosphorus in Commercial Acetylene	ii, 422
NORTH (HORACE). The Assay of Hypophosphorous Acid	ii, 422
CROOK (SIDNEY). [Estimation of] Arsenic in Zinc	ii, 422
RICHARDSON (FREDERIC W.) and WILLIAM KEIGHLY WALTON. Rapid Estimation of Boric Acid in Milk and Cream	ii, 421

	PAGE
RICHARDSON (FREDERIC W.). Combined Estimation of Boric Acid and Fat in Cream	ii, 131
JOHN (W. E. VON). Estimation of Total Carbon in Steel and Ferro-Alloys by Combustion in Oxygen under Pressure	ii, 431
HILPERT (SIGEFRIED). The Estimation of Carbon by Combustion in Moist Oxygen	ii, 432
SINNAT (FRANK S.). Estimation of Carbon Dioxide in Carbonates	ii, 432
GÄRTNER (E. W.). A New Apparatus for the Estimation of Carbon Dioxide	ii, 432
BENBAKER (HOWARD W.). A New Apparatus for the Volumetric Estimation of Carbon Dioxide	ii, 433
KÖNIG (W. A.). A Carbon Dioxide Absorption Bottle	ii, 433
GROSKI (MARYAN). Estimation of Colloids in Arable Soils	ii, 433
LEDREN (RUDOLF VAN DER) and F. SCHNEIDER. New Methods of Soil Analysis and the Estimation of Colloids in Soils	ii, 433
MILLERER (LEDREN). Estimation of Potassium as Platinichloride	ii, 434
WINKLER (LUDWIG W.). Detection of Potassium with Tartaric Acid	ii, 434
MILFORD (LESLIE RUSSELL). Estimation of Lithium	ii, 434
SAINT-SÉVERIN (A.). Estimation of Calcium as Tungstate	ii, 435
GERIN (GABRIEL). Assay of Barium Sulphate in Radiographic Examinations	ii, 435
SPEAR (ELLWOOD B.) and SAMUEL S. STRAHAN. Estimation of Zinc by Electroanalysis	ii, 435
SACHSE (JULIUS F.). Estimation of Lead in Lead Paints	ii, 435
SCHIRM (OTTO). Separation of Small Quantities of Mercury by Electrolysis	ii, 435
KOHN (MOBITZ) and ALFONS OSTRESETZER. Reactions of Mercuric Compounds	ii, 436
JOHN (W. E. VON). Aluminium Alloys and their Analysis	ii, 436
FISCHL (S.). Alkali-Acidimetric Estimation of Alumina and the Acidimetry of the Free Acid in Aluminium Salts	ii, 436
CRUICK (SIDNEY). [Estimation of] Manganese in Ore, Ferromanganese, Spiegeleisen, etc. Volhard's Method	ii, 437
HAAS (FRITZ). Colorimetric Estimation of Small Quantities of Manganese in Water	ii, 437
MILFORD (LESLIE RUSSELL). A Modified Brusen Valve	ii, 437
CHEMISTS' COMMITTEE OF THE U.S. STEEL CORPORATION. The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Pig Iron	ii, 438
RIECKE (REINHOLD) and RICHARD BETZEL. Estimation of Iron and Titanium in Ceramic Materials	ii, 438
SCHAEFFER (JOHN A.). The Colorimetric Estimation of Iron in Lead and its Oxides	ii, 439
DEMAREST (D. J.). Estimation of Chromium and Vanadium in Steel	ii, 439
PATRICK (WILLBUR W.) and G. C. WILSNACK. A New Volumetric Method for the Estimation of Tin	ii, 439
GAZE (RUDOLF). Estimation of Platinum by Precipitation as Sulphide	ii, 440
SCHMIDT (W.). $\alpha$ -Nitroso- $\beta$ -naphthol as a Precipitant for Palladium	ii, 440
BEKATI (CONSTANTIN I.) and M. A. MIHAIULESCU. New Method of Purification of Paraffin and Modification by its Aid of Marcusson and Meyerheim's Process for Identifying Different Paraffins by means of the Iodine Value	ii, 440
HOLBE (DAVID). Relations between the Temperatures of the Vapour and of the Boiling Liquid in the Case of Mixtures of Hydrocarbons	ii, 440
SCHUMBERGER (KERNST). Vapour Pressure of Naphthalene and its Estimation in the Purification of Coal Gas	ii, 441
BERNAN (S. H.). A New Method for the Estimation of Glycerol	ii, 441
REDMAN (L. V.) and E. O. RHODES. Rapid and Accurate Methods for Estimating Phenol	ii, 441
WEISS (JOHN MORRIS). The Estimation of Phenol in Crude Carbolic Acid and Tar Oils	ii, 442

	PAGE
DODGE (FRANCIS D.). The Estimation of Eucalyptol (Cineole) in Essential Oils	ii, 112
FINCKE (HEINRICH). Estimation of Formic Acid in Foods	ii, 142
LANGFIELD (KEET) and ARTHUR ZEILEIS. Analysis of Mixtures of the Lower Fatty Acids	ii, 443
BASS (ROBERT) and WILHELM WIECHOWSKI. The Purine Content of Blood and Its Estimation	ii, 413
ORBELMAYER (FRITZ), HERGO POPPER, and E. ZAR. Detection of Uric Acid in Blood	ii, 444
KASCHIWABARA (M.). Behaviour of Uric Acid to Zinc Salts	ii, 444
FOLIN (OTTO) and WILLEY DENIS. Colorimetric Estimation of Uric Acid in Urine	ii, 111
BRADLER (CLAYTON) and HENRY P. STEVENS. A Simple All-Glass Extraction Apparatus	ii, 444
BÖMER (ALDOIS) and R. LIMPFRICH. Glycerides of Fats and Oils. VI. The Theoretical Basis of Polenske's "Difference" Number	ii, 444
VCAFLART (L.). Analysis of Altered Milks	ii, 445
GRAAFF (WILLEM C. DE) and (MILC.) and A. SCHAAPE. Estimation of Proteins in Milk (by Formaldehyde Titration)	ii, 445
RYNG (IVAR). Estimation of Sugar. II.	ii, 445
BANG (IVAR). A Method of Microchemical Estimation of Certain Constituents of the Blood	ii, 446
BREYERDORFER (PAUL). Estimation of Sugars by the Kjeldahl-Bertrand Method	ii, 447
SANFELICI (RICCARDO). Chemical Estimation of Lactose in Milk	ii, 447
MUTTELER (C. F.). Estimation of Sugars in Foods (Honey, Confectionery, Jams, etc.)	ii, 447
SPECHER (FRIEDRICH) and OTTOKAR FALLADA. Inversion of Raw Sugar Solutions with Ammonium Chloride	ii, 448
AVOGET (A.). Estimation of Starch and Dextrin in Sugar Products, Confectionery, etc.	ii, 448
HUMBARD (W. S.). Difficulties in the Colorimetric Estimation of Vanillin	ii, 448
FOLIN (OTTO) and WILLEY DENIS. A New Colorimetric Method for the Determination of Vanillin in Flavouring Extracts	ii, 449
SAMMET (O.). Estimation of Acetone in Urine	ii, 449
MARRIOTT (W. McKIM). Estimation of Acetone Substances in Blood and Tissues by Micro-methods	ii, 450
TENSMANN (OTTO). Applied Plant Microchemistry. VII. Microchemistry and Microsublimation of Some Methane Derivatives	ii, 150
RHODES (F. H.). The Detection and Estimation of Cyanogen and Hydrogen Cyanide	ii, 450
GREENWALD (ISIDOR). Estimation of Creatine and Creatinine in Diabetic Urines	ii, 450
HOMER (Miss ANNIE). The Colour Reactions of Certain Indole Derivatives and their Significance with regard to the Glyoxylic Reaction	ii, 451
AUYENRIETH (WILHELM) and ALBERT FINK. Some Colorimetric Estimations: Rowntree and Geraghty's Method for Diagnosing the Kidneys; the Estimation of Thiocyanates in Saliva and of Iodine in Urine	ii, 451
BOGDANDY (STEFAN VON). Estimation of Pepsin	ii, 151
RETTAN (ROBERT F.) and R. H. M. HARDISTY. New Reagent for Detecting Blood	ii, 452
RAEHER (J. B.). Application of the Ammonium Carbonate Method for the Estimation of Humus in Hawaiian Soils	ii, 452
ROHLAND (PAUL) and V. MEYSAHN. Estimation of Colloids in Effluents containing Sugar	ii, 452

# INDEX OF AUTHORS' NAMES

## IN TRANSACTIONS AND ABSTRACTS

### A.

Abderhalden, E., and P. Hirsch, i, 548.  
 Abderhalden, E., and A. E. Lampé, i, 547.  
 Abderhalden, E., A. E. Lampé, and E. S. London, i, 550.  
 Abderhalden, E., and A. Weil, i, 450.  
 Abel, E., and G. Baum, ii, 398.  
 Adams, A. See B. Moore.  
 Adler-Herzmark, J., i, 500.  
 Agostinelli, C., i, 459.  
 Aktien-Gesellschaft für Anilin-fabrikation, i, 519.  
 Alberda van Ekenstein, W., and J. J. Blanksma, i, 445.  
 Alexandrov, D. K., i, 443.  
 Amagat, E. H., ii, 382.  
 Ambroz, i, 568.  
 Angeli, A., and B. Valori, i, 533.  
 Armstrong, E. F. See H. E. Armstrong.  
 Armstrong, H. E., E. F. Armstrong, and E. Horton, i, 575.  
 Armstrong, H. E., and J. V. Eyre, ii, 391.  
 Artmann, P., ii, 413.  
 Artmann, P., and J. Preisinger, ii, 436.  
 Aubel, E. van, ii, 357.  
 Auepurgner, L. See O. Wallach.  
 Auguet, A., ii, 448.  
 Austin, J. H., and A. I. Ringer, i, 566.  
 Autenriech, W., and A. Funk, ii, 451.

### B.

Bach, A., i, 543.  
 Badische Anilin- & Soda Fabrik, i, 438, 453, 476, 519.  
 Bagard, P. See A. Wahl.  
 Baig, I., i, 552, 553; ii, 445, 446.  
 Barabanov, A. See G. G. Povarnin.

Barbieri, P. See G. Pighini.  
 Bargellini, G., i, 469.  
 Barker, G., and A. J. Ewins, i, 529.  
 Barker, T. V., and J. E. Marsh, TRANS., 837.  
 Barie, M., ii, 499.  
 Barrett, W. H. See H. Hartley.  
 Barrio y Fernandez, J. See J. Muñoz del Castillo.  
 Bass, R., and W. Wiechowski, i, 413.  
 Bauer, E. See A. Haller.  
 Baum, G. See E. Abel.  
 Baur, E., i, 143.  
 Beadle, C., and H. P. Stevens, ii, 411.  
 Beauffour, H., i, 166, 167.  
 Becker, P. See H. Decker.  
 Beckmann, E., and R. Hanslian, ii, 462.  
 Beckmann, E., and H. Lindner, ii, 359.  
 Beniers, E. See E. Wedekind.  
 Beresin, W. I., i, 566.  
 Bernardini, L., and P. Galluccio, i, 379.  
 Berner, M., i, 569.  
 Berthelot, A., and D. M. Bertrand, i, 569.  
 Berthelot, D., and H. Gaudechon, ii, 369.  
 Bertram, S. H., ii, 411.  
 Bertrand, D. M. See A. Berthelot.  
 Betzel, E. See R. Riecke.  
 Beyersdorfer, P., ii, 417.  
 Bianchi, G., i, 489.  
 Bianu, E., ii, 371.  
 Bielecki, J., and V. Henri, ii, 363.  
 Billy, M., ii, 3-7.  
 Biltz, W., ii, 494.  
 Binder, K. See R. F. Weinland.  
 Blaise, E. E., i, 414.  
 Blanch, E., i, 377.  
 Blanksma, J. J. See W. Alberda van Ekenstein.



Blumann, A., and O. Zeitschel, i, 455.  
 Bodroux, F., i, 440; ii, 358.  
 Bomer, A., i, 441.  
 Bomer, A., and R. Limprich, i, 442; ii, 444.  
 Bogdandy, S. von, i, 549; ii, 426, 451.  
 Bohart, G. S. See A. F. Rogers.  
 Bohn, G. See (Mme.) A. Drzewina.  
 Bokorny, T., i, 569, 571.  
 Bone, W. A., ii, 398.  
 Bongiovanni, C., i, 539.  
 Borowikov, G. A., i, 571.  
 Bosshard, E., and W. Grob, ii, 428.  
 Boulud, R. See R. Lépine.  
 Bordillon, R., TRANS., 791.  
 Bourquelot, E., and M. Bridel, i, 498.  
 Bourquelot, E., and E. Verdon, i, 542.  
 Bonfield, W. R., ii, 383.  
 Bradley, H. C., i, 556.  
 Bragg, W. H., ii, 373.  
 Bramley, A. See J. C. Philip.  
 Brand, H., ii, 409.  
 Brauns, F. See E. Fischer.  
 Brewster, J. F. See H. Lenchs.  
 Bridel, M. See E. Bourquelot.  
 Briner, E., ii, 395.  
 Brossa, G. A., i, 549.  
 Brown, O. W., and A. R. Nees, ii, 410.  
 Browning, H., jun. See F. B. Power.  
 Brubaker, H. W., ii, 433.  
 Buisson, H., and C. Fabry, ii, 361.  
 Buisson, H. See also C. Fabry.  
 Burgstaller, S., ii, 391.  
 Butavand, F., ii, 374.  
 Bywaters, H. W., and A. R. Short, ii, 546.

## C.

Cabella, M., i, 555.  
 Cady, W. G., ii, 380.  
 Campo y Cerdan, A. del, ii, 425.  
 Calugăreanu, D., i, 538.  
 Carbone, D. See G. Fighini.  
 Cardwell, D. See M. O. Forster.  
 Cassella & Co., L., i, 516.  
 Cavel, L., ii, 428.  
 Chablay, E., i, 438.  
 Chadwick, J., and A. S. Kussell, ii, 372.  
 Chapin, H. C., ii, 387.  
 Chapman, A. C., TRANS., 775.  
 Charrier, G., and G. Ferreri, i, 535.  
 Chaudier, J., ii, 268.  
 Chemische Fabrik von F. Heyden, i, 512.  
 Chemische Fabrik Griesheim-Elektron, i, 533.

Chemists' Committee of the U. S. Steel Corporation, ii, 438.  
 Cobet, R., i, 550.  
 Colani, A., i, 444.  
 Coma y Roca, F., ii, 427.  
 Commessmann, H. See M. Freund.  
 Cooper, E. A., i, 538.  
 Corbett, D., i, 558.  
 Corriez, L., i, 512.  
 Costeau, N. See E. Reugade.  
 Crook, S., ii, 430, 437.  
 Curme, G. O., jun. See J. Stieglitz.  
 Curtius, T., and A. Semper, i, 472.  
 Cuthbertson, C., ii, 357.  
 Cuthbertson, C., and (Mrs.) M. Cuthbertson, ii, 358.  
 Cuthbertson, (Mrs.) M. See C. Cuthbertson.  
 Czyhlarz, E. von, A. Fuchs, and O. von Furth, i, 557.

## D.

Dakin, H. D., and H. W. Dudley, i, 565.  
 Damiens, A. See P. Lebeau.  
 D'Ans, J., ii, 408.  
 Darapsky, A., i, 520.  
 Davidsohn, H., i, 545.  
 Davis, L. H., and A. D. Emmett, i, 551.  
 Davis, M. See E. V. McCollum.  
 Decker, H., i, 571.  
 Decker, H., and P. Becker, i, 517.  
 Delépine, M., ii, 411.  
 Demassieux, (Mme.) N., ii, 409.  
 Demjanov, N. J., i, 439.  
 Demjanov, N. J., and M. Dojarenko, i, 451.  
 Demolon, A., i, 579.  
 Demoreest, D. J., ii, 439.  
 Dennis, L. M., ii, 424.  
 Dennis, L. M., and W. J. O'Brien, ii, 430.  
 Denis, W. See O. Folin.  
 Dittler, E. See C. Doelter.  
 Djadkow, See N. Zuntz.  
 Dodge, F. D., ii, 442.  
 Doelter, C., and E. Dittler, ii, 419.  
 Dojarenko, M. See N. J. Demjanov.  
 Doll, M. See A. Wahl.  
 Dominici, H., (Mme.) S. Laborde, and A. Laborde, i, 562.  
 Donau, J., ii, 424.  
 Dormann, K. See O. Piloty.  
 Dreser, H., i, 563.  
 Drew, C. H., i, 567.  
 Drzewina, (Mme.) A., and G. Bohn, i, 557.

Dachandieri, Fürst von. See  
N. Zuntz.  
Dubrisay, R., ii, 388.  
Ducelliez, F. See L. Gay.  
Dudley, H. W. See H. D. Dakin.  
Duffout, A., ii, 406.  
Dunn, J. S., i, 560.  
Durieux, O., i, 445.

# E.

Efremov, N. N. See N. S. Kur-  
nakov.  
Eger, G., ii, 403.  
Eichholz, W. See K. Marck.  
Eisner, F. See O. Ruff.  
Emmett, A. D. See L. H. Davis.  
Engelard, R., and F. Kutacher,  
i, 529.  
Enklaar, C. J. See J. Stark.  
Kras, K. See F. Kunczell.  
Rdman, C. C., ii, 390.  
Euler, H. von, and D. Johansson,  
i, 568.  
Evans, A. J. See G. Barger.  
Eyre, J. V. See H. E. Armstrong.

# F.

Fabry, C., and H. Buisson, ii, 362.  
Fabry, C. See also H. Buisson.  
Fallada, O. See F. Strohmeyer.  
Falta, W., and L. Zehner, ii, 376.  
Farbenfabriken vorm. F. Bayer  
& Co., i, 455, 456, 457, 467, 482, 494,  
498, 513.  
Farbwerke vorm. Meister, Lucius,  
& Brüning, i, 457, 458, 493, 518,  
519, 542.  
Fedorov, E. S. v., ii, 393.  
Fedorov, S. See N. Schilov.  
Ferrari, G. See G. Charrier.  
Feylis, (Mile.) E., ii, 381.  
Finch, G., ii, 429.  
Fincke, H., ii, 442.  
Findlay, A., ii, 397.  
Fischer, A. See J. Stark.  
Fischer, E., and F. Brannus, i, 501.  
Fischer, E., and K. Freudenberg,  
i, 479.  
Fischer, E., and H. O. L. Fischer,  
i, 477.  
Fischer, E., and K. Zach, i, 445.  
Fischer, H. O. L. See E. Fischer.  
Fischl, S., i, 465; ii, 436.  
Fleischer, K. See M. Freund.  
Florentin, D., ii, 425.

Fokin, S. A., i, 442; ii, 399.  
Folin, O., and W. Denis, ii, 444, 449.  
Fomin, W., and N. Sochanski, i, 438.  
Forcrand, R. de, ii, 413.  
Forsén, L. See R. Willstätter.  
Forster, M. O., and D. Cardwell,  
TRANS., 861.  
Francesconi, L., and E. Sernagiotto,  
i, 495.  
Fraude, W. See M. Scholtz.  
Fresenius, H., ii, 401, 427.  
Freudenberg, K. See E. Fischer.  
Freund, M., i, 502.  
Freund, M., and H. Commessmann,  
ii, 504, 506.  
Freund, M., and K. Fleischer, i, 502.  
Freund, M., and H. Hammel, i, 509.  
Freund, M., and R. Lachmann,  
i, 507.  
Freund, M., and D. Steinberger,  
i, 510.  
Freund, M., and E. Zorn, i, 511.  
Friedel, G., ii, 421.  
Fry, H. S., ii, 363.  
Frycz, K., and S. Tolloczko, ii, 380.  
Fuchs, A. See E. von Czychlarsz.  
Furth, O. von. See E. von Czychlarsz.  
Funk, A. See W. Autenrieth.  
Funk, C., i, 557.

# G.

Gaither, E. W., ii, 432.  
Gallo, G., ii, 413.  
Galluccio, F. See L. Bernardini.  
Ganassini, D., i, 449; ii, 370.  
Gasser, H. S., and A. S. Loevenhart,  
i, 543.  
Gaudechon, H. See D. Berthelot.  
Gay, L., ii, 382, 383.  
Gay, L., and F. Ducelliez, ii, 387.  
Gaye, R., ii, 440.  
Gedroiz, K. K., i, 578.  
Geiger, H., and E. Marsden, ii, 371.  
Gesellschaft für Chemische In-  
dustrie in Basel, i, 169.  
Ghiglieno, M., i, 521.  
Ghrgea, E., ii, 392.  
Givens, M. H., and A. Hunter, i, 558.  
Glausser, R. T., ii, 403.  
Glenk, K. See J. König.  
Glover, W. H. See T. M. Lowry.  
Glund, W., TRANS., 940.  
Goris, A., M. Mascré, and C. Vis-  
chniac, i, 576.  
Gorski, A. I., i, 439, 462.  
Gorski, M., ii, 433.  
Goupil, R., i, 567.  
Graff, W. C. de, and A. Schaap,  
ii, 445.

Grafe, E., i, 547, 548.  
 Grassi, U., ii, 395.  
 Green, A. G., TRANS., 925.  
 Green, A. G., and F. M. Rowe,  
 TRANS., 897.  
 Greenwald, L., ii, 450.  
 Grey, E. C., i, 552.  
 Grob, W. See E. Bosshard.  
 Grübler, A. von. See A. Kossovich.  
 Gros, O., i, 552.  
 Grüneisen, E., ii, 377.  
 Grünin, G., ii, 435.  
 Guy, J. S., E. J. Schaeffer, and  
 H. C. Jones, ii, 362.

## H

Haas, F., ii, 437.  
 Hamäläinen, J., i, 497.  
 Haller, A., and E. Bauer, i, 488.  
 Haller, R., i, 495.  
 Hammel, H. See M. Freund.  
 Hamsik, A., i, 540.  
 Hanemann, H., ii, 412.  
 Hansen, A., i, 577.  
 Hanslian, R. See E. Beckmann.  
 Harden, A., i, 568.  
 Hardisty, R. H. M. See R. F. Rutten.  
 Hart, E. B., and H. Steenbock,  
 i, 550.  
 Hart, E. B. See also E. G. Hastings,  
 and H. Steenbock.  
 Hartley, H., and W. H. Barrett,  
 TRANS., 786.  
 Hasenbaumer, J. See J. König.  
 Hasselbalch, K. A., ii, 379.  
 Hastings, E. G., and E. B. Hart,  
 i, 567.  
 Hawkins, A. C., ii, 422.  
 Hedenburg, O. F. See H. G. Wells.  
 Heide, R. von der. See N. Zuntz.  
 Heilmann, B., and W. Marckwald,  
 ii, 374.  
 Hemmelmayr, F. von, i, 468.  
 Henderson, L. J., and W. W. Palmer,  
 i, 558.  
 Henjes, F. See O. Wallach.  
 Henri, V., and R. Wurmser, ii, 369.  
 Henri, V. See also J. Bjelock.  
 Herold, P. See J. Scheiber.  
 Hoesch, N. A., ii, 390.  
 Hevesy, G. v., ii, 376.  
 Hewitt, J. A., i, 547.  
 Hewitt, J. T. See R. Meldola.  
 Hildebrandt, A. See F. Kunczell.  
 Hildebrandt, W. F., ii, 418.  
 Hildebrandt, W. F., and H. E.  
 Merwin, ii, 420.  
 Chulipert, S., ii, 432.  
 Chulipert, S. V., i, 468.

Hirsch, P. See E. Abderhalden.  
 Hoenen, P. H. J., ii, 394.  
 Hoesch, K., i, 474.  
 Holde, D., ii, 440.  
 Homer, (Mis) A., ii, 451.  
 Honda, K., and H. Takagi, ii, 381.  
 Horst, C. See E. Wedekind.  
 Horton, E. See H. E. Armstrong.  
 Hondas, J., i, 551.  
 Howe, P. E. See H. T. Leo.  
 Hubbard, W. S., ii, 448.  
 Hueck, W. See L. Wacker.  
 Hunter, A. See M. H. Givens.

## I

Ibele, J., i, 575.  
 Immeudorff, H., i, 580.  
 Isaac, (Mis) F., ii, 392.  
 Istrati, C. I., and M. A. Mihailescu,  
 i, 493; ii, 440.  
 Istrati, C. I., and C. Teodorescu,  
 i, 437.

## J

Jaquerod, A., and M. Tourpaian,  
 ii, 401.  
 Jerach, W. See O. Ruff.  
 Jochem, O. See E. Wedekind.  
 Johansson, D. See H. von Euler.  
 John, W. E. von, ii, 431, 438.  
 Johnson, T. B., and Z. Z. Zee,  
 i, 521.  
 Jones, H. C. See J. S. Guy.  
 Jovitschitsch, M. Z., ii, 429.

## K

Kahu, M. See N. Stadtmüller.  
 Karzag, L. See J. Plesch.  
 Kardos, M. See C. Liebermann.  
 Kaschiwabara, M., ii, 444.  
 Kay, F. W., and A. Picot, TRANS.  
 947.  
 Keetman, B. See J. Plesch.  
 Kehrman, F., i, 522.  
 Killig, F., ii, 423.  
 Kilpi, S., ii, 397.  
 Kirschbaum, H. See J. Stark.  
 Kisch, B., i, 561.  
 Klappert, L. See A. Michaelis.  
 Kildefeld, G., i, 555.  
 Klein, See N. Zuntz.  
 Klemm, G., ii, 423.  
 Kloppe, K. See J. Scheiber.  
 Knapp-Lenz, E. von, and E. P. Pick,  
 i, 551.

- Koch, F. C., i, 554.  
 König, J. J. Hasenbaumer, and K. Gluck, i, 578.  
 Koenig, W. A., ii, 433.  
 Kohn, M., and A. Ostersetzer, ii, 436.  
 Kopaczewski, L., i, 541.  
 Kossel, A., and F. Weiss, i, 539.  
 Kossowicz, A., i, 571, 572.  
 Kossowicz, A., and L. von Gröfller, i, 568.  
 Krasovski, N., i, 498.  
 Kremers, F. See H. Meerwein.  
 Krüner, A., ii, 383.  
 Kschischkowsky, K., i, 556.  
 Kummerer, D. See F. Weigert.  
 Kunckell, F., K. Eras, A. Hildebrandt, and E. Müller, i, 458.  
 Karnakov, N. S., and N. N. Efremov, ii, 388.  
 Karnakov, N. S., S. F. Shemtshushni, and V. Tararin, ii, 419.  
 Kusnetzov, P., ii, 391, 400, 403.  
 Kutscher, F. See R. Engeland.
- L.**
- Laborde, A. See H. Dominici.  
 Laborde, (Mme.) S. See H. Dominici.  
 Lachmann, R. See M. Freund.  
 Lampe, A. E. See E. Abderhalden.  
 Lange, M., i, 516.  
 Langenscheidt, F., i, 457.  
 Langheld, K., and A. Zeileis, ii, 443.  
 Laqueur, E., i, 546, 547.  
 La Rosa, M., ii, 361.  
 Larsson, K. O., ii, 428.  
 Lassieur, A., i, 444.  
 Lannoy, L., and R. Oechelin, i, 557.  
 Lautenschläger, L. See H. Sieveking.  
 Leavitt, S., i, 447.  
 Lebeau, P., and A. Damiens, i, 437.  
 Lebeau, P., and M. Picon, i, 438.  
 Lebedev, A. von, i, 568.  
 Leeden, R. van der, and F. Schneider, ii, 433.  
 Lénard. See E. Schreiber.  
 Leo, H. T., and P. E. Howe, i, 555.  
 Lepine, R., and R. Boulod, i, 558.  
 Leuchs, H., and J. F. Brewster, i, 449.  
 Levallois, F. See P. de Vilmorin.  
 Levne, P. A., and G. M. Meyer, i, 544.  
 Levy, P. See J. Stark.  
 Lidholm, H., i, 451.  
 Liebermann, C., and M. Kardos, i, 476.  
 Liebreich, E., and F. Spitzer, ii, 413.  
 Limpricht, R. See A. Boner.  
 Lindner, H. See E. Beckmann.  
 Lipp, F. See J. Stark.  
 Lockemann, G., and F. Lucius, i, 481.  
 Loch, A., i, 543.  
 Loewenhardt, A. S. See H. S. Gasser.  
 Loewenhardt, E., ii, 404.  
 Lombard, M., ii, 429.  
 London, E. S. See E. Abderhalden.  
 Longobardi, E., ii, 368.  
 Lowry, T. M., and W. H. Glover, Trans., 913.  
 Lucius, F. See G. Lockemann.
- M.**
- Maass, T. A., and J. Pliesch, i, 583.  
 McCollum, E. V., i, 549.  
 McCollum, E. V., and M. Davis, i, 551.  
 McCollum, E. V., and H. Steenbock, i, 549.  
 McMaster, L., i, 444.  
 Manchot, W., ii, 403.  
 Marcellet, (Mme.) and H. Marcellet, i, 440.  
 Marcellet, H. See (Mme.) Marcellet.  
 Marckwald, W. See B. Heilmann.  
 Marcusson, J., i, 441.  
 Marenine, N. A., ii, 399.  
 Markoff, I. von. See N. Zuntz.  
 Matley, J. See J. H. Vincent.  
 Matquina, M. See E. Moles.  
 Marriott, W. M., ii, 450.  
 Marsden, E. See H. Geiger.  
 Marsh, J. E., and W. C. Rhymes, Trans., 751.  
 Marsh, J. E. See also T. V. Barker.  
 Mascré, M. See A. Garis.  
 Masing, H., i, 439.  
 Mason, G., i, 574.  
 Mathers, F. C., ii, 491.  
 Matignon, C., ii, 395.  
 Mayer, E., i, 558.  
 Mayer, P., i, 564.  
 Mazzé, P., i, 567.  
 Mazzotto, D., ii, 468.  
 Meerwein, H., F. Kremers, H. Probst, and R. Splittesgarb, i, 485.  
 Meillère, G., ii, 434.  
 Meisenheimer, J., i, 447.  
 Meldola, R., and J. T. Hewitt, Trans., 876.

Meneguzzi, K., i, 562.  
 Menten, (Miss) M. L. See L. Michaelis.  
 Merck, E., and W. Eichholz, ii, 374.  
 Merrill, G. P., ii, 424.  
 Merwin, H. E. See W. F. Hillebrand.  
 Metzener, W., ii, 375.  
 Menthen, A., ii, 385.  
 Meyer, F., ii, 408.  
 Meyer, G. M. See P. A. Levene.  
 Meyer, H., and F. Staffen, i, 530.  
 Meyer, K. H., and A. Sander, i, 489.  
 Meyer, K. H., and K. Zahn, i, 455, 536.  
 Meyer, R., i, 493.  
 Meyssah, V. See P. Rohland.  
 Michaelis, A., and L. Klappert, i, 526.  
 Michaelis, A., and A. Schäfer, i, 524.  
 Michaelis, A., and W. Titius, i, 527.  
 Michaelis, L., and (Miss) M. L. Menten, i, 540.  
 Michaelis, L., and P. Rona, ii, 379.  
 Michel, F., ii, 426.  
 Mihailescu, M. A. See C. I. Istrati.  
 Milford, L. R., ii, 434, 437.  
 Mitscherlich, E. A., and W. Stimmermacher, i, 580.  
 Minra, S., i, 544, 564.  
 Moles, E., M. Marquina, and G. Santos, ii, 390.  
 Moore, B. E. Whitley, and A. Adams, i, 556.  
 Moore, B., E. Whitley, and A. Webster, i, 456.  
 Moorhouse, V. H. K., i, 552.  
 Morgan, G. T., and J. Reilly, TRANS., 508.  
 Moroschkina, O. I., i, 444.  
 Müller, E. See F. Kunczell.  
 Müller, K. See O. Wallach.  
 Muñoz del Castillo, J., ii, 376.  
 Muñoz del Castillo, J., and J. Barrio Fernandez, ii, 376.  
 Murat, M. See P. Sabatier.  
 Muscelfeann, C., ii, 382.  
 Muttelet, C. F., ii, 417.

## N.

Nacken, A., ii, 361.  
 Nees, A. R. See O. W. Brown.  
 Neuberg, C., i, 561.  
 Nicola, P., ii, 427.  
 Nielsen, O., ii, 407.  
 Nierenstein, M., i, 501.  
 Noetting, E., and J. Saas, i, 522.  
 Nolan, T. J., and S. Smiles, TRANS., 901.  
 North, H., ii, 439.

## O.

Obermayer, F., H. Popper, and E. Zak, ii, 444.  
 O'Brien, W. J. See L. M. Dennis.  
 Oechslein, K. See L. Launoy.  
 Ochsner de Coniuck, W., and A. Raynaud, i, 440.  
 Oettingen, W. F. von. See H. Wich-haus.  
 Oppe, A., i, 534.  
 Oppermann, F. See F. Rolly.  
 Orlov, N. A., ii, 421.  
 Ost, H., i, 446.  
 Osterhout, W. J. V., i, 571.  
 Ostersetzer, A. See M. Kuhn.

## P.

Page, H. J. See R. H. A. Plimmer.  
 Palladin, V. J., i, 570.  
 Palmer, W. W. See L. J. Henderson.  
 Panzer, T., i, 541.  
 Pappenheim, A., and J. Plesch, i, 563.  
 Parker, A, TRANS., 934.  
 Parnas, J., i, 554.  
 Parravano, N., ii, 392, 415.  
 Paschen, F., ii, 361.  
 Pasternack, R. See P. Rahn.  
 Patrick, W. A. See W. H. Walker.  
 Patrick, W. W., and G. C. Wilsnack, ii, 439.  
 Pavlov, B. V. See V. V. Tschelincev.  
 Pecker, H., ii, 407.  
 Peschek, E., ii, 460.  
 Philip, J. C., and A. Bramley, TRANS., 795.  
 Pick, E. P. See E. von Knafel-Lenz.  
 Picou, M. See P. Lebeau.  
 Pietet, A. See F. W. Ray.  
 Pieroni, A., and E. Tonndorf, ii, 393.  
 Pighini, G., P. Barbieri, and U. Carbone, i, 551.  
 Pignoni, L., i, 564.  
 Piloty, O., i, 500.  
 Piloty, O., and E. Dormann, i, 539.  
 Piloty, O., and J. Stock, i, 512.  
 Pina de Rubies, S., ii, 424.  
 Pinnow, J., ii, 398.  
 Pintti, A., ii, 419.  
 Piwnikiewicz, H., ii, 388.  
 Plesch, J., L. Karczag, and R. Keetman, i, 563.  
 Plesch, J. See also T. A. Maass and A. Pappenheim.  
 Plimmer, R. H. A., and H. J. Page, i, 445.

- Plotnikov, V. A., and V. E. : Rolly, F., and F. Oppermann, i, 559.  
 Rokotjan, ii, 378.  
 Pohl, R., and P. Pringsheim, : Rona, P., and D. Takahashi, i, 544.  
 ii, 374, 377. : Rona, P. See also L. Michaelis.  
 Pepper, H. See F. Obermayer. : Rosenbloom, J. See N. Stadt-  
 Povarnin, G. G., and A. Barabanov, : muller.  
 i, 576. Rosenmund, K. W., i, 462.  
 Povarnin, G. G., and N. Shuravlev, : Roth, W. A., and H. Wallasch,  
 i, 576. ii, 384.  
 Power, F. B., and H. Browning, jun., : Rowe, F. M. See A. G. Green.  
 i, 574. Rudolph, O., ii, 424.  
 Porzi-Escot, M. E., ii, 409. Ruff, O., F. Eisner, and W. Jeroch,  
 Prats Aymerich, J., ii, 492. ii, 416.  
 Preisinger, J. See P. Artmann. Ruff, O., and F. W. Tschirch, ii, 416.  
 Pring, J. N., ii, 350. Ruhlmann, W., ii, 323.  
 Pringsheim, P. See K. Pohl. Role, A. See J. S. Thomas.  
 Prebst, H. See H. Meerwein. Russ, F., ii, 493.  
 Proumen, H. J., ii, 373. Russell, A. S. See J. Chadwick.  
 Puxeddu, E., i, 469. Ruttan, R. F., and R. H. M.  
 Pyman, F. L., TRANS., 817, 852. Hardisty, ii, 152.

Q.

- quartaroli, A., ii, 416.

R.

- Rabe, P., i, 513.  
 Rabr, P., and R. Pasternack, i, 513,  
 514.  
 Radlberger, L., i, 450.  
 Raper, H. S., i, 546.  
 Rather, J. B., ii, 452.  
 Raynaud, A. See W. Echsner de  
 Coninck.  
 Redman, L. V., and E. O. Rhodes,  
 ii, 441.  
 Reichard, C., ii, 394.  
 Reilly, J. See G. T. Morgan.  
 Rengade, E., and N. Costeau.  
 ii, 495.  
 Rhodes, E. O. See L. V. Redman.  
 Rhodes, F. H., ii, 450.  
 Rhynes, W. C. See J. E. Marsh.  
 Richardson, F. W., ii, 431.  
 Richardson, F. W., and W. K.  
 Walton, ii, 431.  
 Riecke, R., and R. Betzel, ii, 438.  
 Riechel, J. D., i, 469.  
 Riegel, E. R. See C. R. Sanger.  
 Rieger, J. B. See W. Salant.  
 Ringer, A. I. See J. H. Austin,  
 J. E. Sweet, and A. E. Taylor.  
 Riva, A., i, 566.  
 Rogers, A. F., and G. S. Bohart,  
 ii, 419.  
 Rohland, P., ii, 412.  
 Rohland, P., and V. Meyssah, ii, 452.  
 Rokotjan, V. E. See V. A. Plot-  
 nikov.

S.

- Saas, J. See E. Noelting.  
 Sabatier, P., and M. Murat, i, 468.  
 Saccharin-Fabrik Aktiengesell-  
 schaft vorm. Fahlberg, List &  
 Co., i, 459.  
 Sacher, J. F., ii, 435.  
 Saint-Sernin, A., ii, 495.  
 Sakaki, C., 554.  
 Salant, W., and J. B. Rieger,  
 i, 547.  
 Salikowski, E., i, 562, 565.  
 Sammet, O., ii, 449.  
 Sandelin, A. E., i, 469.  
 Sander, A. See K. H. Meyer.  
 Sanfelici, R., ii, 447.  
 Sanger, C. R., and E. R. Riegel,  
 ii, 495.  
 Santos, G. See E. Moles.  
 Scala, A., ii, 409.  
 Schaap, A. See W. C. de Graaff.  
 Schaffer, A. See A. Michaelis.  
 Schaeffer, E. J. See J. S. Guy.  
 Schaeffer, J. A., ii, 439.  
 Scheiber, J., and P. Herald, i, 490.  
 Scheiber, J., K. Kloppe, and K.  
 Schnabel, i, 491.  
 Schilling, H., i, 493.  
 Schlor, N., and S. Fedotov, ii, 371.  
 Schliecher, A., ii, 411.  
 Schlubach, H. See O. Wallach.  
 Schlumberger, E., ii, 441.  
 Schmidt, W., ii, 410.  
 Schnabel, K. See J. Scheiber.  
 Schneider, F. See R. van der  
 Leeden.  
 Schmidewind, W., i, 579.  
 Schoeller, W. R., ii, 415.  
 Scholtz, M., i, 529.

Scholtz, M., and W. Fraude, i, 514.  
 Schreiber, E., and Léonard, i, 544.  
 Schryver, S. B., and C. Singer, i, 561.  
 Schulze, B., i, 580.  
 Schumm, O., ii, 435.  
 Scott, A., TRANS., 847.  
 Selivanov, F. F., ii, 406, 407.  
 Sellei, J., i, 566.  
 Semper, A. See T. Curtius.  
 Sernagiotto, E. See L. Francesconi.  
 Seyewetz, A., i, 492.  
 Shaw, T. P., i, 545.  
 Shemtschushni, S. F. See N. S. Kurnakov.  
 Short, A. R. See H. W. Bywaters.  
 Shuravlev, N. See G. G. Povarnin.  
 Siebeck K., i, 553.  
 Sievking, H., and L. Lauten-schläger, ii, 372.  
 Silbermintz, W., ii, 423.  
 Simmermacher, W. See E. A. Mitscherlich.  
 Singer, C. See S. B. Schryver.  
 Sinnatt, F. S., ii, 432.  
 Sissner, A., ii, 412.  
 Slater, A., i, 568.  
 Smiles, S. See T. J. Nolan.  
 Smith, H., ii, 360.  
 Smits, A., ii, 393.  
 Sochanski, N. See W. Fomin.  
 Spear, E. B., and S. S. Strahan, ii, 435.  
 Sperber, J., ii, 400.  
 Spitzer, F. See E. Liebreich.  
 Splittegarb, R. See H. Meerwein.  
 Stadtmüller, N. M. Kahn and J. Rosenbloom, i, 559.  
 Staffen, F. See H. Meyer.  
 Stark, J., A. Fischer and H. Kirsch-haun, ii, 360.  
 Stark, J., and P. Levy, ii, 366.  
 Stark, J., and P. Lipp, ii, 365.  
 Stark, J., W. Stenbing, C. J. Enklaar, and P. Lipp, ii, 363.  
 Stassano, H., i, 545.  
 Steck, H., i, 548.  
 Steenbock, H., and E. B. Hart, i, 550.  
 Steenbock, H. See also E. B. Hart, and E. V. McCollum.  
 Steinberger, D. See M. Freund.  
 Stenstrom, T., i, 564.  
 Steubing, W. See J. Stark.  
 Stevens, H. P. See C. Beadle.  
 Stieglitz, J., and G. O. Curme, jun., ii, 398.  
 Stock, J. See O. Piloty.  
 Stoermer, R., i, 437.  
 Strahan, S. S. See E. B. Spear.  
 Straus, F., i, 455.  
 Strecker, W., i, 440.

Strohmer, F., and D. Fallada, ii, 448.  
 Sugden, S., ii, 382.  
 Sweet, J. E., and A. I. Ringer, i, 565.  
 Sy, A. P., ii, 429.

## T.

Takagi, H. See K. Honda.  
 Takahashi, D. See P. Roux.  
 Tanaka, Y., i, 446.  
 Tararin, V. See N. S. Kurnakov.  
 Taverne, H. J., i, 443.  
 Taylor, A. E., and A. I. Ringer, i, 548.  
 Tedesco, H., i, 447.  
 Teodoresco, E. C., i, 542.  
 Teodorescu, C. See C. I. Istrati.  
 Thiel, A., ii, 395, 396, 423.  
 Thomas, J. S., and A. Rule, TRANS., 871.  
 Tinkler, C. K., TRANS., 885.  
 Tittus, W. See A. Michaelis.  
 Tolloczko, S. See K. Frycz.  
 Tonnioli, E. See A. Pieroni.  
 Tourpaian, M. See A. Jaquerod.  
 Tsakalotos, D. E., i, 521.  
 Tschelincev, V. V., and B. V. Pavlov, i, 461.  
 Tschernik, G. P., ii, 421.  
 Tschirch, F. W. See O. Ruff.  
 Tschirvinski, P. N., ii, 421.  
 Tschitschibabin, A. E., i, 467.  
 Tneker, W. S., ii, 378.  
 Tunnmann, O., ii, 450.

## U.

Ujedinov, M. N. See N. D. Zelinski.  
 Ullmann-Goldberg, I., i, 495.  
 Urban, K., i, 449.

## V.

Valiaschko, N. A., ii, 367.  
 Vafari, B. See A. Angeli.  
 Varvaro, V., i, 570.  
 Vanbel, W., i, 519.  
 Venditori, D., i, 451.  
 Vendl, A., ii, 420.  
 Verdon, E. See E. Bourquelot.  
 Vesterberg, A., ii, 406.  
 Viguier, P. L., i, 444.

Vilmorin, P. de, and F. Levallois,  
i, 577.  
Vincent, J. H., and J. Marley,  
ii, 369.  
Vischniac, C. See A. Goris.  
Vuaflart, L., ii, 445.

W.

Wacker, L., and W. Hueck, i, 554.  
Wahl, A., and P. Bagard, i, 519.  
Wahl, A., and M. Doll, i, 473, 531.  
Wahl, W. A., i, 488; ii, 404.  
Walker, E. E., ii, 368.  
Walker, W. H., and W. A. Patrick,  
ii, 427.  
Wallach, O., L. Augspurger, F.  
Henjes, and R. Müller, i, 482.  
Wallach, O., L. Augspurger, and  
H. Schlubach, i, 452.  
Wallasch, H. See W. A. Roth.  
Walton, W. K. See F. W. Richard-  
son.  
Webster, A. See B. Moore.  
Wedekind, E., and E. Beniers,  
i, 476.  
Wedekind, E., C. Horst, and O.  
Jochem, ii, 414.  
Weldlein, E. R., i, 502.  
Weigert, F., and L. Kummerer,  
ii, 370.  
Weil, A. See E. Abderhalden.  
Weimarn, P. P. von, ii, 394.  
Weimer, G., ii, 367.  
Weinland, R. F., and K. Binder,  
i, 458.  
Weiss, F. See A. Kossel.  
Weiss, J. M., ii, 442.  
Wellisch, J., i, 529.

Wells, H. G., and O. F. Hedenburg,  
i, 562.  
Wernicke, R., i, 451.  
Whipple, G. H., i, 550.  
Whitby, G. S., i, 575.  
Whitley, E. See B. Moore.  
Wiechowski, W. See R. Bass.  
Wienhaus, H., and W. F. von  
Oettingen, i, 474.  
Willstätter, R., and L. Forsén,  
i, 499.  
Wilsar, H., ii, 359.  
Wilsnack, G. C. See W. W. Patrick.  
Winkler, L. W., ii, 434.  
Woodyatt, R. T., i, 559.  
Wurmser, R. See V. Henri.  
Wyrenboff, G., ii, 381.

Z.

Zach, K. See E. Fischer.  
Zahn, K. See K. H. Meyer.  
Zak, E. See F. Obermayer.  
Zambonini, F., ii, 419.  
Zee, Z. Z. See F. B. Johnson.  
Zehner, L. See W. Falta.  
Zeileis, A. See K. Langheld.  
Zeitschel, O. See A. Blumann.  
Zelinski, N. D., and M. N. Ujedinov,  
i, 466.  
Zellner, J., i, 572, 573.  
Zeynek, R. von, i, 499; ii, 359.  
Zorn, E. See M. Freund.  
Zubov, P. V., ii, 385.  
Zuntz, N., E. von der Heide,  
Klein, I. von Markoff, Fürst  
von Dschandieri, and Djadkow,  
i, 577.

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VOL. XCVIII (ABSTR., 1910).

Page.	Line.	
i, 536	23	for "Pinacene Transformation" read "Pinacolin Transformation."





# CONTENTS.

xvii

	PAGE
JANDER (G. DRUGE) and H. W. WINTER. [Detection of] Antipyrine in Toxicological Analysis . . . . .	ii, 355
GERLIN (GABRIEL). Estimation of Morphine in Opium and its Preparations . . . . .	ii, 355
ANDREASSEN (EMIL) and DIONYS FUCHS. Estimation of <i>L</i> -Tyrosine in Proteins . . . . .	ii, 355
KOBER (PHILIP A.). Nephelometry in the Study of Proteases. II. . . . .	ii, 355
ARNOLD (VINENZ). Arnold's Nitroprusside Reaction in Urine . . . . .	ii, 356
ROHLAND (PAUL). Estimation of Colloids in Effluents . . . . .	ii, 356
GALLI-VALERIO (B.) and M. BERNARD. A Rapid Method of Determining the Quality of Drinking Waters . . . . .	ii, 356

# INDEX OF AUTHORS' NAMES

## IN TRANSACTIONS AND ABSTRACTS

### A.

- Abderhalden, E., i, 419.  
 Abderhalden, E., and D. Fuchs, i, 409.  
 Abderhalden, E., and A. E. Lampe, i, 420.  
 Abderhalden, E., and A. Weil, i, 420.  
 Adams, L. H. See J. Johnston.  
 Ageton, C. N. See P. L. Gile.  
 Agulhon, H. See G. Bertrand.  
 Aitchison, L. See P. Ibbotson.  
 Aktien-Gesellschaft für Anilinfabrikation, i, 366.  
 Alexandrowicz, J. S., i, 419.  
 Algar, J. See H. Ryan.  
 Allbee, A. G. See D. A. Hahn.  
 Ambroun, H., ii, 321.  
 Anderson, E., i, 341.  
 André, G., i, 431.  
 Arlunzov, A. E., i, 347.  
 Arlunzov, A. E., and A. V. Kartaschov, i, 333.  
 Arlunzov, A. E., and V. M. Tichovinski, i, 338, 338.  
 Arnold, F., i, 396.  
 Arnold, V., ii, 356.  
 Atack, F. W., ii, 345.  
 Aubel, E. van, ii, 294.  
 Aubel, F., and H. Pick, i, 419.  
 Autenrieth, W., and A. Fnnk, ii, 355.  
 Auwers, K. von, ii, 261.  
 Auwers, K. von, and M. Schmidt, i, 228.  
 Babb, J., i, 411.  
 Backer, H. J., i, 346.  
 Badische Anilin & Soda-Fabrik, i, 349, 373.  
 Bahr, P., ii, 290.  
 Bamberger, E., and E. Reber, i, 379.  
 Bamberger, M., and K. Kruse, ii, 278.  
 Barbier, P., and R. Locquin, i, 307, 337, 341.  
 Barendrecht, H. P., ii, 349.  
 Barsickow, M., i, 123.  
 Bart, H., i, 415.  
 Bartholomäus, E. See H. Fischer.  
 Baskov, A. V. See N. A. Puschin.  
 Benedicks, C., ii, 367.  
 Bergner, E. See A. Sieverts.  
 Berry, A. J., ii, 322.  
 Berthelot, A., i, 423.  
 Berthelot, D., and H. Gauderchon, ii, 267.  
 Berthoud, A., ii, 305, 309.  
 Bertrand, G., and H. Agulhon, i, 423.  
 Bickel, A., and M. Pavlov, i, 424.  
 Biddle, H. C., ii, 311.  
 Bielecki, J., and V. Henri, ii, 263.  
 Bierry, H., and (Mlle.) L. Fandard, i, 429.  
 Bielecki, R. See A. Rosenheim.  
 Bishop, E. S. See W. D. Bonner.  
 Blankman, J. J., i, 353.  
 Block, E. A., ii, 262.  
 Boden, E. See H. Schade.  
 Böseken, J., P. Hasselbach, W. J. P. Pelle, and (Mlle.) S. van der Tas, i, 335.  
 Böseken, J., C. E. Klammer, and J. G. de Vaagt, i, 350.  
 Böseken, J., and G. H. van Sonden, i, 331.  
 Boehm, E., i, 426.  
 Boehringer & Söhne, C. F., i, 385.  
 Bötters, O. See K. Woldenstien.  
 Bokorny, T., i, 428.  
 Boll, M., ii, 265.  
 Bonner, W. D., and E. S. Bishop, ii, 335.  
 Bornand, M. See B. G. Valerio.  
 Bos, J. L. M. van der H. van den, ii, 338.

### B.

Gaswell, M. C., ii, 331.  
 Gouganit, J., i, 366.  
 Bourquetot, E., H. Hérissay, and  
 Mc Bride, i, 428.  
 Bourquetot, E., and J. Coirre, i, 416.  
 Bradbury, W. A., and F. Owen,  
 ii, 339.  
 Brand, K., and A. Wirsing, i, 496.  
 Briesch. See R. Lrspiean.  
 Bridel, M., i, 434.  
 Bridel, M. See also E. Bourquetot.  
 Briner, E., and A. Kuhn, ii, 320.  
 Briner, E., and Z. Pytkoff, ii, 317.  
 Bronsted, J. N., ii, 295.  
 Broniewski, W., ii, 288.  
 Buchner, E., and W. Weigand,  
 ii, 376.  
 Buglia, G., i, 418.  
 Burger, A. See A. Heiduschka.  
 Burkser, E. See M. Tanatar.  
 Burmann, J., i, 432.  
 Barrell, G. A., i, 329.

C.

Cain, J. C., A. K. Macbeth, and  
 A. W. Stewart, TRANS., 586.  
 Cannon, W. B., and H. Lyman,  
 i, 426.  
 Carvajal, (Mlle.). See H. Le  
 Chatelier.  
 Chemische Fabrik von Friedr.  
 Heyden, i, 385, 416, 417.  
 Chemische Fabrik von Karszty.  
 Wolff & Cie, i, 376.  
 Chesneau, G., ii, 317.  
 Chick, (Miss) H., and C. J. Martin,  
 i, 169.  
 Chodat, R., and K. Schweizer,  
 i, 111.  
 Chouquard, L., i, 423.  
 Canician, G. L., and P. Silber,  
 i, 350.  
 Clarke, F. W., ii, 313.  
 Clinton, S. See J. B. Ekeley.  
 Clouta, M., i, 424.  
 Clough, G. W. See A. McKenzie.  
 Cohen, E., and J. F. Kromer, ii, 315.  
 Cohn, R., ii, 352.  
 Coirre, J. See E. Bourquetot.  
 Collin, H., and A. Schenck, ii, 319.  
 Collins, H., ii, 313.  
 Conzen, J. See M. Poppe.  
 Connelley, H. P., ii, 332.  
 Conen, A., and H. Montan, ii, 288.  
 Crane, W., and H. Pringle, i, 417.  
 Crodner, F., ii, 286.  
 Crother, H. L., and H. McCombie,  
 TRANS., 560.

Cunningham, (Miss) M. See C. Dutton.  
 Cushman, A. S., and E. B.  
 Wettengel, ii, 315.

D.

Dalimier, R., i, 425.  
 Damicus, A. See F. Lebeau.  
 Danysz, J., ii, 279.  
 Demarest, D. J., ii, 311, 312.  
 Demonssy, E. See L. Maquenne.  
 Dewey, F. D., ii, 319.  
 Dezanb, S., i, 419.  
 Dhar, N., ii, 319.  
 Dietrich, M., ii, 311.  
 Ditz, H., ii, 329.  
 Dohle, W., and B. Kassow, i, 496.  
 Dorce, C., and (Miss) M. Cunn-  
 ington, TRANS., 577.  
 Duane, W., and O. Schener, ii, 279.  
 Duffour, A., i, 398.

E.

Edgar, E. C. See A. Holt.  
 Ekeley, J. B., and S. Clinton, i, 395.  
 Elrod, E. See A. Koenig.  
 Endell, K. See A. Smits.  
 Enklaar, C. J., i, 339.  
 Escalas, R., and H. Koepke, i, 331.  
 Evans, C. L., i, 418.

F.

Fabius, K., ii, 276, 277.  
 Fackel, V., ii, 327.  
 Falk, K. G., i, 433; ii, 241.  
 Fandard, (Mlle.) L. See H. Riechy.  
 Farbenfabriken vorm. F. Bayer  
 & Co., i, 342, 343, 355, 361, 369, 367,  
 373, 375, 393, 463, 491.  
 Farbenwerke vorm. Meister, Lucius &  
 Brüning, i, 361, 372, 373, 393, 399.  
 401, 412, 415, 416.  
 Faneau, A. See G. Massol.  
 Fedorov, E. S., ii, 355, 366.  
 Fedorov, P. P., and V. Iljinsky,  
 ii, 323.  
 Ferber, H. von. See Erich M. Her.  
 Feys, C., and E. Tassilly, ii, 332.  
 Fiechter, E., and E. Meiler, ii, 347.  
 Fildray, A., and T. Williams,  
 TRANS., 666.  
 Fingerling, G., i, 429.  
 First, J. E. See A. Holt, and  
 J. E. Myers.  
 Fischer, E., and E. Henz, ii, 317.  
 Fischer, E., and O. Priess, ii, 285.

- Fischer, H., and E. Bartholomäus, i, 409.  
 Fischer, H., and H. Röse, i, 382.  
 Fitzgerald, R. See H. Ryan.  
 Fletcher, J., and D. Tyrer, TRANS., 517.  
 Florentin, D. See A. Kling.  
 Fol, J. G., ii, 301.  
 Fomin, W., and N. Sochanski, i, 321.  
 Fonrobert, E. See C. D. Harries.  
 Forster, A. See E. Fromm.  
 Forster, M. O., TRANS., 662.  
 Fort, M., ii, 306, 311.  
 Fosse, R., i, 432.  
 Fouard, E., ii, 304.  
 Fraenkel, H. See J. Howitz.  
 Frank, J., ii, 307.  
 Frankland, P. F., TRANS., 713.  
 Frieder, W., ii, 337.  
 Friedrichs, F., ii, 316.  
 Fritsch, O. See G. Heller.  
 Fromm, E., A. Forster, F. Schafer, and B. von Scherschewitzki, i, 357.  
 Fuchs, D. See E. Abderhalden.  
 Funk, A. See W. Antenrieth.
- G.**
- Gaither, E. W., ii, 338.  
 Galli-Valerio, B., and M. Bornand, ii, 356.  
 Garben, O. See O. Stark.  
 Gassmann, T., ii, 329.  
 Gaudechon, H. See D. Berthelot.  
 Gavin, W., i, 421.  
 Gersten, E. See O. Ruff.  
 Gesellschaft für Chemische Industrie, i, 383.  
 Gile, P. L., and C. X. Ageton, i, 436.  
 Godchet, M., and F. Tahoury, i, 348.  
 Goldschmidt, H., and H. K. Grini, ii, 284.  
 Golodetz, A., ii, 304.  
 Gooch, F. A., and D. U. Hill, ii, 319.  
 Gottstein, G. See J. Koenigsberger.  
 Graebe, C., ii, 313.  
 Grengg, R., ii, 278.  
 Grini, H. K. See H. Goldschmidt.  
 Grode, J., and E. J. Lesser, i, 420.  
 Grosser, P., i, 424.  
 Guareschi, L., ii, 313, 333.  
 Guerin, G., ii, 355.  
 Guillet, L., and A. Portevin, ii, 326.  
 Gurwitsch, L., ii, 295.
- H.**
- Hahn, D. A., and A. G. Allbee, i, 367.  
 Halban, H. von, i, 355.  
 Halban, H. von, and A. Kirsch, ii, 312.  
 Hale, W. J., and L. Thorp, i, 369.  
 Halla, F., ii, 326.  
 Hantzsch, A., i, 393.  
 Hantzsch, A., and I. Lifschitz, ii, 264.  
 Harries, C. D., i, 342.  
 Harries, C. D., and E. Fonrobert, i, 380.  
 Haschek, E., and O. Hönigschmid, ii, 268.  
 Haselhoff, E., i, 429.  
 Hasselbach, P. See J. Boeseken.  
 Hauser, O., and H. Muschner, i, 363.  
 Hauser, O., and W. Steger, ii, 290.  
 Haynes, E., ii, 328.  
 Heidelberger, M. See R. Willstätter.  
 Heiduschka, A., and A. Baizer, ii, 351.  
 Heller, G., and O. Fritsch, i, 345.  
 Henderson, W. E., and H. B. Weiss, ii, 327.  
 Heine, E. See F. Fischer.  
 Henning, E., ii, 289.  
 Henri, V., and M. Landau, ii, 267.  
 Henri, V. See also J. Dieckmann.  
 Hepner, E. E. See F. W. Heyl.  
 Hepp, E., R. Uhlenuth, and F. Römer, i, 374.  
 Hérissey, H. See R. Bourquelot.  
 Herring, P. T., i, 421.  
 Herrmann, K., i, 133.  
 Herrmann, F. See S. Hilpert.  
 Herz, O. See R. Weissgerber.  
 Heyl, F. W., F. E. Hepner, and S. K. Loy, i, 386.  
 Higgins, S. H., ii, 311.  
 Hill, A. V., i, 422.  
 Hill, D. U. See F. A. Gooch.  
 Hillen, G. H., i, 378.  
 Hilpert, S., and F. Herrmann, ii, 289.  
 Hintikka, S. Y. See G. Komppa.  
 Hirz, O., i, 417.  
 Hönigschmid, O., ii, 268.  
 Hönigschmid, O. See also E. Haschek.  
 Hofer, H. See M. Popp.  
 Hoffmann, C., i, 427.  
 Hogley, C. F., ii, 273.  
 Holt, A., E. C. Edgar, and J. R. Firth, ii, 330.  
 Holt, A., and J. E. Myers, TRANS., 532.  
 Horton, F., ii, 272.  
 Howitz, J., H. Fraenkel, and I. Schroeder, i, 388.

Howitz, J., and O. Köpke, i, 392.  
 Howitz, J., and J. Philipp, i, 391.  
 Hühneret, E. See S. Kostytshev.

## I.

Ibbotson, F., and L. Aitchison, ii, 344, 346.  
 Ilijinsky, V. See P. P. Fedot'ev.  
 Irvine, J. C., and J. P. Scott, TRANS. 564, 575.  
 Ivanov, V. N., ii, 340, 343.

## J.

Jacot, E., ii, 271.  
 Järvinen, K. K., ii, 293.  
 Johnson-Blohm, G., ii, 351.  
 James, C., ii, 323.  
 James, J. H., i, 329.  
 Jegorov, M. A. See E. Winterstein.  
 Johns, C. O., i, 404.  
 Johnson, T. R., and E. F. Kohlmann, i, 402.  
 Johnson, T. B., and B. H. Nicolet, i, 398.  
 Johnston, J., and L. H. Adams, ii, 290.  
 Jobilois, P., i, 318.  
 Jona, T., i, 422.  
 Jones, H. C. See E. J. Schaeffer.  
 Jones, W. J., ii, 309.  
 Jong, A. W. K. de, i, 384.  
 Joyinet, See Köhler.  
 Jürisch, K. W., ii, 298.

## K.

Kyllau, A., ii, 270.  
 Kallé & Co., i, 401, 495.  
 Karrer, P., i, 412.  
 Kartachov, A. V. See A. A. Ailonzov.  
 Kaufmann, H., ii, 264.  
 Keller, K., i, 403.  
 Kemmer, J., TRANS., 613.  
 Kiliani, H., i, 381.  
 King, V. L. See R. Willstätter.  
 Kirkby, P. J., and J. E. Marsh, ii, 278.  
 Kirsch, A. See H. von Halban.  
 Kita, G., i, 410.  
 Kitt, E., ii, 319.  
 Klauer, C. E. See J. Borsche.  
 Kleemann, R. D., ii, 301.  
 Klein, P., ii, 262.  
 Klein, A. See R. Weissgerber.  
 Kling, A., and D. Florentin, ii, 309.  
 Klungenberg, K. L. See F. Ullmann.  
 Kloster, H. S. van, ii, 330.

Knaff-Lenz, E. von, and E. P. Pick, i, 419.  
 Knoll & Co., i, 341.  
 Kober, P. A., ii, 355.  
 Köhler, M. Marquetryrol, and Joyinet, ii, 334.  
 Koenig, A., and E. Elöd, ii, 316.  
 König, W., and R. Schreckenbach, i, 400.  
 Koenigsberger, J., and G. Gottstein, ii, 280.  
 Köpke, H. See R. Escales.  
 Köpke, O. See J. Howitz.  
 Koffler, M., ii, 271.  
 Köhlschütter, V., ii, 257.  
 Köhlschütter, V., and H. Schacht, ii, 287.  
 Köhlschütter, V., and T. Toropoff, ii, 255.  
 Köhlschütter, V., T. Toropoff, and W. Pfandler, ii, 256.  
 Kohlmann, E. F. See T. B. Johnson.  
 Kolosovski, X. A., ii, 308.  
 Kolowrat, L., ii, 274.  
 Komppa, G., and S. V. Hintikka, i, 375.  
 Kouscheg, A. von, i, 426.  
 Korolev, R. See E. Winterstein.  
 Kostytshev, S., E. Hühneret, and A. Schelounov, i, 434.  
 Kozniowski, T., i, 428.  
 Kraft, F. See R. Weissgerber.  
 Kraum, H. E., ii, 331.  
 Krapivin, S., ii, 310, 325.  
 Krishnappa, H. V., ii, 339.  
 Kroner, J. F. See E. Cohen.  
 Kruse, K. See M. Bamberger.  
 Kuhne, A. See E. Reimer.  
 Kunkell, P., and G. Claus, i, 359.  
 Kylin, H., i, 435.

## L.

Lamp, A. E. See E. Abderhalden.  
 Landau, M. See V. Henri.  
 Landet, G. D., and H. W. Winter, ii, 355.  
 Lohau, P., and A. Daniels, ii, 349.  
 Le Chatelier, H., and Mlle. Crémieux, ii, 291.  
 Lehmann, F., ii, 351.  
 Lehmann, K. B., i, 425.  
 Leopold, G. H., i, 436.  
 Leischen, B., and Brusch, i, 353.  
 Lesser, E. J., i, 423.  
 Lesser, E. J. See also J. Grode.  
 Levy, S. L. See S. Ruhemann.  
 Lewin, L., i, 332.  
 Ley, H., and F. Maunichen, i, 346.  
 Liesegang, R. E., ii, 307.  
 Lifschitz, L. See A. Hautschel.

Lifschutz, I. ii, 350.  
 Linhart, G. A., ii, 310.  
 Lipman, C. B., and H. F. Pressey,  
 ii, 335.  
 Litterscheid, F. M., ii, 351.  
 Loequin, R., i, 341.  
 Loequin, R. See also P. Barbier.  
 Lob, W., i, 343.  
 Logginov, N. A., i, 332.  
 Lorenz, R., ii, 281.  
 Loy, S. K. See F. W. Heyl.  
 Luther, R., and A. Nikolopoulos,  
 ii, 263.  
 Lyman, H. See W. B. Cannon.

## M.

Macbeth, A. K. See J. C. Cain.  
 McCombie, H. See H. L. Crowther.  
 McCoy, H. N., and C. H. Viol, ii, 271.  
 McKenzie, A., and G. W. Clough,  
 TRANS., 687.  
 McMillen, R. H., ii, 333.  
 MacNider, G. M., i, 311.  
 Mannehen, F. See H. Ley.  
 Maetzel, J. See R. Mohlau.  
 Mailhe, A., i, 355.  
 Mailhe, A. See also P. Sabatier.  
 Maquenne, L., and E. Demoussy,  
 i, 429.  
 Marcelin, R., ii, 294.  
 Marek, J., ii, 337.  
 Marquoyrol, M. See Kohler.  
 Marrs, L. E. See F. J. Metzger.  
 Marsh, J. E. See P. J. Kirkby.  
 Martin, C. J. See (Miss) H. Chick.  
 Martin, W. See O. Ruff.  
 Massol, G., and A. Faucon, ii, 264.  
 Mathews, A. P., ii, 399.  
 Mayer, A., and G. Schaeffer, i, 124.  
 Medigreeann, F., i, 425.  
 Medigreeann, F. See also E.  
 Paterno.  
 Meimberg, E., and P. Winzen, ii, 318.  
 Menschukin, E. N., i, 351, 352.  
 Mentz, H. See M. Papp.  
 Merck, E., i, 334, 343.  
 Merriman, R., TRANS., 628.  
 Metzger, F. J., and L. E. Marrs,  
 ii, 344.  
 Meyer, A., i, 391.  
 Meyer, H., and K. Steiner, i, 368.  
 Meyer, R., ii, 261, 313.  
 Meyer, R. J., and J. Wuorinen,  
 ii, 323.  
 Meyer, S., ii, 267.  
 Micheltner, K., and H. Steinmetz,  
 ii, 321.  
 Millar, C. E., ii, 337.  
 Mines, G. R., i, 422.

Mirande, R., i, 432.  
 Miodziejowski, A., ii, 506.  
 Mohlau, R., and J. Maetzel, i, 341.  
 Moll van Charante, J., i, 344.  
 Monton, H. See A. Cotton.  
 Moycho, V., i, 424.  
 Muller, E. See F. Fichter.  
 Müller, Erich, and H. von Feil,  
 ii, 334.  
 Müller, J. See T. Zincke.  
 Mumford, E. M., TRANS., 645.  
 Murat, M. See P. Sabatier.  
 Muschner, H. See O. Hauser.  
 Myers, J. E., and J. B. Firth, ii, 322.  
 Myers, J. E. See also A. Holt.

## N.

Navassart, E., i, 383.  
 Neumann, R., ii, 352.  
 Nicolet, B. H. See T. B. Johnson.  
 Nierenstein, M., i, 382.  
 Nikolopoulos, A. See R. Luther.  
 Normand, L. See P. Pascal.

## O.

Oehrmayer, E., ii, 333.  
 Oehsner de Coninck, W., and A.  
 Raynaud, i, 333.  
 Olsson, O., ii, 328.  
 Oppermann, F. See F. Bolly.  
 Owen, P. See W. A. Bradbury.  
 Oxley, A. E., ii, 288.

## P.

Pavi, W. See R. Wolfenstein.  
 Palladin, V. I., and Z. N. Tolstaj,  
 i, 439.  
 Paneth, F., ii, 273.  
 Pantanello, E., and G. Severini,  
 i, 455.  
 Parker, C. E., ii, 315.  
 Pascal, P., and L. Normand, ii, 261,  
 304.  
 Paschke, F. See E. Wedekind.  
 Paterno, E., and F. Medigreeann,  
 i, 409.  
 Pavlov, M. See A. Bickel.  
 Pawlowski, E., i, 398.  
 Peacock, D. H., TRANS., 629.  
 Pelaton, H., ii, 330.  
 Pella, W. J. P. See J. Rosseken.  
 Penev, C. M., ii, 359.

Perkin, A. G. *TRANS.*, 650.  
 Perkins, A. E., ii, 314.  
 Pfandler, W. See V. Kohlschütter.  
 Phillips, J. See J. Howitz.  
 Pick, E. P. See E. von Knaffl-  
 Lenz.  
 Pick, H. See F. Auerbach.  
 Platonikov, J., ii, 265.  
 Pontio, ii, 317.  
 Poppe, M., J. Contzen, H. Hofel,  
 and H. Mentz, ii, 336.  
 Portevin, A. See L. Guillet.  
 Potter, H. M. See M. A. Rosenhoff.  
 Pazzi-Escott, M. E., ii, 332, 341.  
 Pratalonge, U., ii, 282.  
 Pressey, H. F. See C. R. Lipman.  
 Prantschnikov, D., ii, 339.  
 Priess, O. See F. Fischer.  
 Pringle, H. See W. Cramer.  
 Prunhomme, M., ii, 298.  
 Puschkin, N. A., and A. V. Baskov,  
 ii, 319.  
 Pytkoff, Z. See E. Riner.

R.

Rakovski, A. V., ii, 302, 303.  
 Rassow, B. See W. Dohle.  
 Raynaud, A. See W. Ecksner de  
 Coninck.  
 Reber, E. See E. Bamberger.  
 Rebul, G., ii, 303.  
 Reichard, C., ii, 254.  
 Reuter, C. See E. Winterstein.  
 Risse, F. See F. W. Semmler.  
 Rief, H., i, 421.  
 Robinson, H. See E. Rutherford.  
 Romer, F. See L. Hepp.  
 Rose, H. See H. Fischer.  
 Rothund, P., ii, 302, 338, 356.  
 Rolly, F., and F. Oppermann, i, 425.  
 Rosenhoff, M. A., and H. M. Potter,  
 i, 311.  
 Rosenberg, I. See F. W. Semmler.  
 Rosenheim, A., and R. Blüchli,  
 i, 413.  
 Roenthaler, L., i, 410, 411; ii, 254.  
 Rossen, A. van, i, 379.  
 Rosset, H., ii, 353.  
 Roth, W. A., and R. Stoermer, ii, 296.  
 Rousseaux, E., and M. Siroi, ii, 351.  
 Ruff, O., and E. Gersten, ii, 294, 325.  
 Ruff, O., and W. Martin, ii, 329.  
 Ruhemann, S., and S. I. Levy,  
*TRANS.*, 551.  
 Russell, A. S., ii, 270, 274.  
 Ruszkowski, M. See A. Tschirch.  
 Rutherford, E., and H. Robinson,  
 ii, 269.  
 Ryan, H., and J. Algar, i, 335.  
 Ryan, H., and R. Fitzgerald, i, 383.

S.

Sabatier, P., and A. Mailhe, i, 330.  
 Sabatier, P., and M. Murat, i, 302.  
 Sachanov, A. N., ii, 283.  
 Sborgi, U., ii, 318.  
 Scala, A., ii, 325.  
 Schacht, H. See V. Kohlschütter.  
 Schade, H., and E. Roden, i, 404.  
 Schafer, E. A., i, 421.  
 Schäfer, F. See E. Fromm.  
 Schaeffer, E. J., and H. C. Jones,  
 ii, 282.  
 Schaeffer, G. See A. Mayer.  
 Schaller, W. T., ii, 331.  
 Scheloumov, A. See S. Kostyt-  
 shev.  
 Scherschewitzki, B. von. See E.  
 Fromm.  
 Scherer, O. See W. Duane.  
 Schlechter, C. W., i, 330.  
 Schmidt, M. See K. von Auwers.  
 Scholtz, M., i, 385.  
 Schreckenbach, R. See W. König.  
 Schroeder, E. See J. Howitz.  
 Schröder, F., i, 431.  
 Schweidler, E. von, ii, 271.  
 Schweizer, K. See R. Chadat.  
 Schwenk, K. See W. Weichardt.  
 Scott, J. P. See J. C. Irvine.  
 Seher, J. See J. Stoklasa.  
 Seidler, L., i, 425.  
 Seki, T., i, 436.  
 Semmler, F. W., and F. Risse,  
 i, 369.  
 Semmler, F. W., and I. Rosenberg,  
 i, 377.  
 Senden, G. H. van. See J.  
 Boeseken.  
 Senderens, J. B., i, 312.  
 Sénéchal, A., ii, 328.  
 Sénéchal, A. See also H. Colin.  
 Severini, G. See E. Pantanelli.  
 Shaw, L. I., ii, 283.  
 Sheard, C., ii, 272.  
 Sieverts, A., and E. Bergner,  
 ii, 321.  
 Silber, P. See G. L. Ciamician.  
 Silberzweig, G. See A. Wahl.  
 Simon, F., i, 431.  
 Singh, B. K. *TRANS.*, 604.  
 Siroi, M. See E. Rousseaux.  
 Skórzewski, W., and J. Sohn,  
 i, 427.  
 Smith, H. E., ii, 337.  
 Smith, N., ii, 314.  
 Smith, A., and K. Endell, ii, 318.  
 Sochinski, N. See W. Lemm.  
 Sobby, F., ii, 275.  
 Sohn, J. See W. Skórzewski.  
 Sorkan, W., ii, 301.  
 Southerden, F., ii, 314.



Spence, D., i, 381.  
 Spencer, A. C., ii, 331.  
 Stark, J., ii, 294.  
 Stark, O., and O. Garben, i, 361.  
 Stassano, H., i, 418.  
 Steger, W. See O. Hanser.  
 Steiner, K. See H. Meyer.  
 Steinmetz, H. See K. Mieleitner.  
 Stewart, A. W. See J. C. Cain.  
 Stoermer, R. See W. A. Roth.  
 Stoklass, J., J. Schor, and W. Zdobnický, i, 342.  
 Stollé, R., i, 345.  
 Stoltzenberg, H., i, 345.  
 Strömholm, D., i, 347.  
 Strutt, (Hon.) R. J., ii, 279, 316.  
 Swinne, R., ii, 277.  
 Swinne, R. See also P. Walden.

## T.

Taboury, F. See M. Godchet.  
 Tanatar, M., and E. Burksen, ii, 273.  
 Tas (Mile.) S. van der. See J. Boeseken.  
 Tassilly, E. See C. Föry.  
 Thomas, E. R., TRANS., 594.  
 Thorp, L. See W. J. Hale.  
 Tichvinski, V. M. See A. E. Arbuzov.  
 Tolstaja, Z. N. See V. I. Palladin.  
 Tornpoff, T. See V. Kohlschütter.  
 Treadwell, W. D., ii, 342.  
 Tschirch, A., and M. Ruszkowski, i, 434.  
 Tschirwinski, P. N., i, 348.  
 Thunmann, O., ii, 351.  
 Tyrer, D. See J. Flecken.

## U.

Uerményi, D. See O. N. Witt.  
 Uhlenhuth, R. See E. Hepp.  
 Ulex, G. See F. Kneckell.  
 Ulmann, F., and K. L. Klingenberg, i, 374.

## V.

Vanzetti, B. L., ii, 295.  
 Vereinigte Chinifabriken Zimmer & Co., i, 334.  
 Vernet, C. G., i, 195.  
 Viol, C. H. See H. N. McCoy.  
 Vollhase, E., ii, 353.  
 Voogt, J. G. de. See J. Boeseken.

## W.

Wagenaar, M., ii, 348.  
 Wahl, A., and G. Silberzweig, i, 394.  
 Walden, P., and R. Swinne, ii, 299.  
 Wassiljewa, A., ii, 265.  
 Watson, R. R., TRANS., 548.  
 Watson, H. E., ii, 279.  
 Wedekind, E., and F. Paschke, i, 351.  
 Wehmer, C., i, 432.  
 Weichardt, W., and I. Schwenk, i, 422.  
 Weigand, W. See E. Buchner.  
 Weigert, F., ii, 266.  
 Weil, A. See E. Abderhalden.  
 Weimarn, P. P. von, ii, 307.  
 Weiser, H. B. See W. E. Henderson.  
 Weissenberger, G., ii, 338.  
 Weissgerber, R., O. Herz, A. Klemm, and F. Kraft, i, 387.  
 Weisspfenning, G. See T. Zincke.  
 Wells, H. L., i, 347.  
 Wettengel, E. B. See A. S. Cushman.  
 Wiley, S. W., ii, 314.  
 Williams, H. G., ii, 333.  
 Williams, T. See A. Findlay.  
 Willstätter, R., and M. Heideberger, i, 348.  
 Willstätter, R., and V. L. King, i, 353.  
 Willstätter, R., and T. Wirth, i, 359.  
 Winkler, L. W., ii, 336.  
 Winter, H. W. See G. D. Lander.  
 Winterstein, E., and M. A. Jegorow, i, 433.  
 Winterstein, E., C. Reuter, and R. Korolew, i, 423.  
 Winzer, P. See K. Meimberg.  
 Wirsing, A. See K. Brand.  
 Wirth, T. See R. Willstätter.  
 Witt, O. N., and D. Uerményi, i, 369.  
 Wolfenstein, R., and O. Baders, i, 355.  
 Wolfenstein, R., and W. Pütz, i, 363, 364.  
 Wolfenstein, R., and J. Zeltner, i, 367.  
 Wood, R. W., ii, 262.  
 Wright, R., TRANS., 528.  
 Wuorinen, J. See K. J. Meyer.

## Z.

Zdobnický, W. See J. Stoklass.  
 Zeltner, J. See R. Wolfenstein.  
 Zincke, T., and J. Müller, i, 355.  
 Zincke, T., and G. Weisspfenning, i, 389.

## ERRATA.

## VOL. CII (ABSTR., 1912).

Page.	Line.	
i, 118	11*	for "3:4-Dimethyleneoxychalcone" read "3:4-Methylenedioxychalcone."
i, 118	8*	„ "3:4-Dimethylenoxydihydrochalcone" read "3:4-Methylenedioxydihydrochalcone."

## VOL. CIV (ABSTR., 1913).

i, 129	8*	for "Pathology" read "Pharmacology"
i, 309	3	„ "40" read "46."

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\* From German.



## General and Physical Chemistry.

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**Change in Refractive Index with Temperature.** III. K. GEORGE FALK (*Zeitsch. physikal. Chem.*, 1913, 82, 501-505).—In the two previous papers (A., 1909, ii, 197, 629) an account was given of measurements of the refractive indices of a number of organic liquids. The present paper deals with a theoretical consideration of these results on the basis of new determinations of the atomic refractions by Eisenlohr (A., 1910, ii, 365; 1911, ii, 81). The author compares the observed molecular refractions of the substances *diisomyl*, *n*-heptyl alcohol, *n*-butyric acid, methyl hexyl ketone, *isobutyl* acetate, ethyl *n*-butyrate, and *isomyl* acetate with those calculated from Eisenlohr's atomic refractions. It is shown that for the values at 20° there is a small but generally unimportant difference between the two values. The Lorentz-Lorenz formula is considered. It is written  $(n^2 - 1)/(n^2 + 2)d$ , and the value of  $n$  is calculated from the experimental values of the specific refraction of the substances mentioned above. It is shown that  $a$  varies between 3.6 and 6.9, but the value for the two isomeric substances, *isobutyl* acetate and ethyl *n*-butyrate, is practically the same for the  $\alpha$ ,  $\beta$ , and  $\gamma$ -hydrogen lines and for the *D*-sodium line, and is equal to 4.5 as a mean. J. F. S.

**The Spectrochemistry of Compounds with a *gem*-Dialkyl Group.** KARL VON AUWERS (*Ber.*, 1913, 46, 491-511).—It is found that the presence of a *gem*-dialkyl group in a molecule generally causes a depression of the molecular refraction and dispersion, the effect being most marked when the group is substituted into a conjugation of double linkings; thus ethyl *d*-*ris*-camphorate, ethyl *l*-*trans*-camphorate, and dimethyl *isodehydrocamphorate* (Bredt, A., 1909, i, 498; this vol., i, 338) show such a depression, whilst methyl *d*-*dehydrocamphorate* and ethyl *d*-*dehydrocamphorate*, although containing conjugated double linkings, show no sign of exaltation; ethyl bornylenecarboxylate, in which the dimethyl group is outside the conjugation, exhibits an exaltation. The influence of the *gem*-dimethyl group is less marked when present in a substance of normal spectrochemical behaviour, but becomes more appreciable as the size of the alkyl radicals increases; for example, although ethyl dimethylacetoacetate is normal, a slight depression is observable with ethyl methylethylacetoacetate, and this becomes still more marked with ethyl diethylethylacetoacetate. Especial care was taken to ensure the purity of the last three substances, and hence probably arises some divergence in the figures quoted below from those already published by Brühl (A., 1894, ii, 133). With ethyl malonate, also, the introduction of two ethyl groups or of a methyl and ethyl group has a marked depressing effect, whilst two methyl radicals have no apparent action on the refraction.

The refraction of the following substances was measured for the  
VOL. CIV, ii.

$\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $D$ -lines, but only the value for the last is quoted below.

Methyl *n*-dehydrocamphorate,  $\begin{array}{c} \text{CH}_2\text{C}(\text{CO}_2\text{Me}) \\ | \\ \text{CH}_2\text{C}(\text{CO}_2\text{Me}) \end{array} \text{CMe}_2$  b. p. 132—132.5°/9 mm.,  $D_4^{25}$  1.0915,  $n_D^{25}$  1.47509; ethyl *dl*-dehydrocamphorate, b. p. 145—146°/10 mm.,  $D_4^{25}$  1.0400,  $n_D^{25}$  1.46588; methyl isodehydrocamphorate,  $\begin{array}{c} \text{CH} \cdot \text{CH}(\text{CO}_2\text{Me}) \\ | \\ \text{CH} \cdot \text{CMe}(\text{CO}_2\text{Me}) \end{array} \text{CMe}_2$  b. p. 128—129 mm.,  $D_4^{25}$  1.0852,  $n_D^{25}$  1.46782; ethyl bornylene-carboxylate,  $\begin{array}{c} \text{CH}_2 - \text{CH} - \text{C}(\text{CO}_2\text{Et}) \\ | \\ \text{CMe}_2 \end{array}$  b. p. 122°/16 mm.,  $D_4^{25}$  0.9826,  $n_D^{25}$  1.47604.

Ethyl methylacetoacetate, b. p. 75.5—76.5°/12 mm.,  $D_4^{25}$  1.0008,  $n_D^{25}$  1.42066; ethyl ethylacetoacetate, b. p. 80°/10 mm.,  $D_4^{25}$  0.98531,  $n_D^{25}$  1.42366; ethyl dimethylacetoacetate, b. p. 78°/11 mm.,  $D_4^{25}$  0.9777,  $n_D^{25}$  1.41828; ethyl methyl ethylacetoacetate, b. p. 85°/12 mm.,  $D_4^{25}$  0.9734,  $n_D^{25}$  1.42586; ethyl diethylacetoacetate, b. p. 92—92.5°/9 mm.,  $D_4^{25}$  0.9710,  $n_D^{25}$  1.43266; methylacetoacetate, b. p. 72—72.5°/12 mm.,  $D_4^{25}$  1.0755,  $n_D^{25}$  1.41837; methyl methylacetoacetate, b. p. 80°/20 mm.,  $D_4^{25}$  1.0308,  $n_D^{25}$  1.41629; methyl dimethylacetoacetate, b. p. 74°/15 mm.,  $D_4^{25}$  1.0002,  $n_D^{25}$  1.41789.

Ethyl malonate, b. p. 198—198.6°,  $D_4^{25}$  1.0566,  $n_D^{25}$  1.41508; ethyl methylmalonate, b. p. 201.2—201.4°,  $D_4^{25}$  1.0192,  $n_D^{25}$  1.41369; ethyl dimethylmalonate, b. p. 88.7°/21 mm.,  $D_4^{25}$  0.9910,  $n_D^{25}$  1.41049; ethyl methylethylmalonate, b. p. 102°/17 mm.,  $D_4^{25}$  0.9970,  $n_D^{25}$  1.41896; ethyl diethylmalonate, b. p. 109—110°/21 mm.,  $D_4^{25}$  0.9880,  $n_D^{25}$  1.42516; methyl dimethylmalonate, b. p. 71°/22 mm.,  $D_4^{25}$  1.0591,  $n_D^{25}$  1.41312; methyl diethylmalonate, b. p. 97—98°/22 mm.,  $D_4^{25}$  1.0615,  $n_D^{25}$  1.42528.

D. P. T.

**Arc and Spark Spectrum of Lead.** FRITZ KLEIN (*Zeit. phys. Photochem.*, 1913, 12, 16—30).—These spectra have been re-examined in order to obtain data expressed in terms of the International normal lines. The measurements were made with a Rowland concave grating, the spectrum of the second order being used for the great majority of the lines which covered the region between  $\lambda=7228$  and  $\lambda=2088$ . The recorded data are compared with the results obtained by previous observers. The existence of three groups of ten lines in the arc spectrum, the corresponding members of which show the same difference in frequency on passing from one group to another, is clearly shown by the author's data, which thus confirm the relationship first indicated by Kayser and Runge.

H. M. D.

**Selective Dispersion of Mercury Vapour at the  $\lambda=2536$  Absorption Line.** ROBERT W. WOOD (*Physikal. Zeitsch.*, 1913, 14, 191—195).—Quantitative measurements have been made of the dispersion produced by mercury vapour in the immediate neighbourhood of the mercury line  $\lambda=2536.5$ . The observations were carried

out with mercury vapour, saturated at temperatures between  $34^{\circ}$  and  $58^{\circ}$ , the iron lines of wave-lengths  $\lambda=2535.6$ ,  $\lambda=2536.9$ , and  $\lambda=2539.0$  being submitted to examination. For these three lines, the displacement increases as the wave-length becomes more nearly equal to that of the absorption line, being greatest for the second and least for the third line. The displacement is not proportional to the pressure of the mercury vapour, but increases much less rapidly than this. In the case of the iron line  $\lambda=2535.6$  the displacement was found to increase in the ratio 1:3 when the pressure was raised from 0.0031 to 0.0215 mm., that is, in the ratio 1:7. From this it would appear that the molecules, which are directly responsible for the dispersion in the neighbourhood of the absorption line, are not the normal molecules of mercury. Whether the active molecules are complex aggregates or ionised molecules cannot be determined.

H. M. D.

**Relationship between the Absorption Spectrum and the Constitution of Complex Cobaltammine Salts.** ROBERT LUTHER and ANDREAS NIKOLOPOULOS (*Zeitsch. physikal. Chem.*, 1913, 82, 361—378).—In determining the absorption spectrum of twenty complex cobaltammine salts, the visible portion of the spectrum was measured by a spectro-photometer using a mercury vapour lamp as the source of light, and the ultraviolet portion was measured by Hartley's method using a quartz spectrograph and an iron spark as source of light. The various errors of the method are discussed, and an approximate estimate of their dimensions is made. It is shown that the light absorption is only dependent on the composition of the complex. The replacement of  $\text{NH}_3$  by  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}$ , and  $\text{Br}$  in the complex causes a displacement of the absorption toward the red end of the spectrum. Replacement of  $\text{NH}_3$  by  $\text{NO}_2$  causes a displacement toward the violet end. In accord with the electron theory, the stability of analogous compounds is greater the further the absorption bands extend toward the violet, and the photochemical sensitiveness is greater the steeper the absorption curve.

J. F. S.

**Quantitative Investigation of the Absorption of Ultra-violet Rays by the Fatty Acids and their Esters in Aqueous and Alcoholic Solutions.** JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, 156, 550—552).—In continuation of this investigation (compare this vol., ii. 86) the authors have studied the absorption by the fatty acids and their esters in alcoholic solutions and by sodium formate and acetate in aqueous solutions, and from the results have calculated the molecular coefficients of absorption. The figures are tabulated, and show that the absorption of the ultraviolet rays is almost the same for the esters as for the acids, the absorption of a compound of the type  $\text{C}_n\text{H}_{2n+1}\cdot\text{CO}_2\text{R}$  being determined by the acid group, the alcohol radicle having only a feeble influence. Alcoholic solutions have a stronger absorptive power than aqueous solutions, due probably to the displacement of the absorption bands, in alcoholic solution, towards the red end

of the spectrum. The acids, arranged in ascending absorptive power, are acetic, propionic, formic, butyric, and valeric, and, leaving out formic acid, the absorption increases with addition of  $\text{CH}_2$  to the molecule. No change occurs in the form of the absorption curve, but a displacement of the bands towards the red is produced.

The sodium salts of the acids studied are less absorbent than the acids themselves, probably owing to the greater ionisation of the salts in aqueous solution. W. G.

**Spectrographic Studies in the Anthraquinone Group.** RICHARD MEYER (*Ber.*, 1913, 46, 617. Compare this vol., ii, 168).—The author acknowledges that Formánek has dealt with the anthraquinone dyes in a work entitled "Investigation and Identification of Organic Dye stuffs by means of the Spectroscope," and points out the difference between the aims of this investigation and of his own. II. W.

**Absorption Spectra of Fluorescein, Eosin, Erythrosin, and Rose-Bengal in the Visible and Invisible Regions.** GUSTAV MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1913, [iv], 13, 217—221).—The authors have examined the absorption spectra of fluorescein, eosin, erythrosin, and rose-bengal (dichlorotetraiodofluorescein). In the visible portion the spectra obtained closely resemble one another, giving a band extending over the blue and green portion, the limits of which have been defined with regard to the yellow sodium, green thallium, blue strontium, and violet potassium lines. In the ultra-violet, fluorescein gives three bands between  $\lambda = 260$  and  $\lambda = 335$ , depending on the thickness of the layer; eosin gives only one band between  $\lambda = 325$  and  $\lambda = 345$ , only visible in thickness above 50 mm.; erythrosin and rose-benzal only show a progressive absorption without bands, the latter being much the more powerfully absorptive. All the substances were examined in aqueous solution (concentration, 1 in 10,000). II. W.

**Optical Investigations of Diazo compounds.** ARTHUR HANTZSCH and ISRAEL LIFSCHITZ (*Ber.*, 1913, 46, 414—416. Compare A., 1912, ii, 1116).—Polemical; a reply to Cain (this vol., i, 169). The authors dissent from Cain's views, and reaffirm the correctness of their own interpretation of the phenomena. D. F. T.

**The Theory of Fluorescence.** HUGO KAUFFMANN (*Zeitsch. Elektrochem.*, 1913, 19, 192—196).—Polemical. An answer to Stark (this vol., ii, 2), and a further criticism of Stark's theory of fluorescence (A., 1911, ii, 786). J. F. S.

**The Theory of Fluorescence.** JOHANNES STARK (*Zeitsch. Elektrochem.*, 1913, 19, 196—197).—Polemical. An answer to Kauffmann (see preceding abstract). J. F. S.

**The Theory of Fluorescence.** HUGO KAUFFMANN (*Zeitsch. Elektrochem.*, 1913, 19, 197).—Polemical. An answer to Stark (see preceding abstract). J. F. S.

[Rotation Dispersion.] JON. PLOTNIKOV (*J. pr. Chem.*, 1913, [ii], 87, 236—237).—A note on the author's light filter, the efficiency of which was called into question by Deussen (this vol., ii, 88).

F. B.

**Energy Absorbed and Mass Formed in a Photochemical Reaction.** MARCEL BOLL (*Compt. rend.*, 1913, 156, 691—694).—A mathematical paper, in which the author deduces the following laws: (1) When an absorbent substance is the seat of a chemical reaction the emergent energy decreases according to the exponential function of the thickness of the layer and the concentration at each instant. (2) The mass formed,  $m = (kst)^{\frac{1}{2}} \chi \cdot c H'a$ , where  $s$  = surface,  $t$  = time,  $\chi$  = coefficient of absorption,  $H'a$  = incident energy,  $c$  = concentration. (3) In the case of a bimolecular reaction, Grotthus's law of photochemical absorption does not hold good, there being no ratio between the mass formed and the energy absorbed. W. G.

**Photochemical Behaviour of Colloidal Tungstic Acid.** ALEXANDRA WASSILJEWA (*Zeitsch. wiss. Photochem.*, 1913, 12, 1—15).—If dilute hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes slightly acid, a colloidal solution of tungstic acid is obtained, which in presence of various organic substances, such as formaldehyde, sucrose, dextrose, dextrin, etc., undergoes reduction on exposure to light, with the formation of an intense blue solution. If the undilysed solution is kept for some time, it is found that the above reduction process does not occur when the solution is exposed to light: on raising the temperature, however, the blue reduction products are obtained, as in the case of the freshly prepared colloidal solution.

It is suggested that this is due to the existence of two forms of colloidal tungstic acid, one of which is photochemically sensitive and the other not. The former changes spontaneously into the latter, but the reverse transformation is brought about by a rise of temperature.

The absorption spectra of the two modifications are found to differ appreciably, the region of ultraviolet absorption extending further towards the visible spectrum in the case of the photochemically sensitive modification.

Kinetic experiments have also been made in order to ascertain the nature of the change in which the photochemically active form is converted into the inactive modification. These show that the change proceeds in accordance with the equation for a unimolecular reaction. The rate of transformation was ascertained by measurements of the photochemical activity of the colloidal solution after measured intervals of time. This was effected by exposing the colloidal solution, containing dextrose as reducing agent, to the light from an arc lamp for five minutes, and estimating the amount of the reduction which occurred during this period by titration with a permanganate solution. From the photochemical sensitivities obtained in this way it was possible to ascertain the corresponding concentration of the active form by reference to a curve con-



necting the two quantities, this curve being plotted from data obtained in experiments which were carried out to determine the connexion between the two factors.

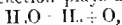
By similar measurements it has been found that a colloidal solution, which had become quite inactive at 7°, regained 31% of its original photochemical activity when heated to 43°, and 81% when heated to 96°. That this is not due simply to an acceleration of the photochemical change with rise of temperature is shown by measurements of the influence of temperature on the reactivity of the freshly prepared colloidal solution. In common with all photochemical reactions, the temperature-coefficient was found to be very small, the velocity increasing by only 1% when the temperature was raised from 8° to 96°.

As regards the chemical relationship between the active and inactive colloids, very little information has been obtained. The spectroscopic data would seem to show that both are colloidal and of similar composition, and it is suggested that the change from the active to the inactive form may consist in the addition of water or in the combination of the tungstic acid with sodium salts according to  $3\text{WO}_3 + \text{Na}_2\text{WO}_4 = \text{Na}_2\text{O} \cdot 4\text{WO}_3$ , which substance was obtained by Sabančev (A., 1897, ii, 456) by subjecting the solution to dialysis.

H. M. D.

**The Activation of Oxygen by Radiation.** FRITZ WEIGERT (*Ber.*, 1913, 46, 815—820).—In order to investigate the photochemical reaction of ozone it was necessary to use a part of the spectrum where ozonisation of oxygen does not occur. This was attained by using a quartz-mercury lamp, and allowing the rays to pass through a layer of air before entering the reaction vessel. The apparatus was similar to that previously used by the author (A., 1912, ii, 715) in the investigation of the decomposition of ozone by ultraviolet light, and the particular reaction used was that between ozone and hydrogen. No trace of hydrogen peroxide was formed (compare Coehn, A., 1910, ii, 608), and there was only an extremely slow reaction in the dark. In ultraviolet light, however, about one-third of the ozone originally present disappeared in two minutes, the disappearance being due to the two reactions:  $2\text{O}_3 = 3\text{O}_2$  and  $\text{H}_2 + \text{O}_3 = \text{H}_2\text{O} + \text{O}_2$ . The total amount of ozone decomposed is proportional to the ozone concentration, whilst the amount of hydrogen oxidised approached asymptotically an upper limit, which was attained at an ozone concentration which was the lower the lower the concentration of the hydrogen. This limit is approximately proportional to the concentration of the hydrogen (compare Clausmann, A., 1910, ii, 608).

The above results indicate that in the activation of oxygen by ultraviolet rays two photochemical reactions occur. In the formation of water from hydrogen and oxygen the oxygen is first ozonised by the short rays, and then reacts with hydrogen under the influence of the long rays. In the photochemical dissociation of water vapour a further photochemical reaction plays a part, namely,



which is affected by the short rays. The complicated relations observed by Cohn (*loc. cit.*) are thus explained.

It is possible that the deviation of the nitric oxide equilibrium from the position calculated thermochemically is due to the photochemical action between nitrogen and ozone, the latter being formed from oxygen by the ultraviolet rays, as, for example, in the experiments of Fischer and Hene (this vol., ii, 317). T. S. P.

**Absorption of the Ultraviolet Rays by Acetylene.** VICTOR HENRI and MARC LANDAU (*Compt. rend.*, 1913, 156, 697—699).—A study of the ultraviolet absorption spectra of acetylene, first, in a gaseous state at the ordinary temperature, under a pressure of one tenth to one atmosphere, using a thickness of 40 cm. of gas, and secondly in alcoholic solution. In the first case there are three distinct groups of bands. The first extends from  $\lambda$  3157 to 2880; the second beginning to appear at  $\lambda$  2960, and being most marked between  $\lambda$  2800 and 2500; the third extends from  $\lambda$  2327.5 to 2236.4, and is in turn capable of resolution into a series of very fine bands. Between  $\lambda$  2500 and 2327.5 acetylene in the gaseous state under the given conditions shows no sensible absorption. In alcoholic solution acetylene presents only one very broad band, commencing at  $\lambda$  2850 and attaining a maximum at  $\lambda$  2631. The ultraviolet absorption by acetylene commences approximately at the region where the solar ultraviolet spectrum ends. W. G.

**The Inversion of Sucrose by Ultraviolet Rays.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 156, 468—470).—A résumé of work already published (compare A., 1910, ii, 813; 1912, i, 750, ii, 1120; this vol., i, 16, ii, 4), and a reply to Bierry, Henri, and Ranc (this vol., ii, 4). W. G.

**A Lævulose Actinometer for Ultraviolet Rays. Influence of Concentration on the Rate of Photochemical Action.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 156, 707—710).—A 10 per cent. aqueous solution of lævulose can be used to give a direct measure of the intensity of the radiation, the volume of the gas evolved being directly proportional to the time for any given radiation, and inversely proportional to the (distance)<sup>2</sup>. Further, for dilute solutions (4.5 to 18 grams per litre) the velocity of the reaction is proportional to the concentration, whilst for strong solutions (720 to 1080 grams per litre) it is constant and independent of the concentration. These facts are best explained on the hypothesis that the velocity of reaction is proportional to the quantity of light absorbed per unit of time. W. G.

**The Most Recent Value for the Atomic Weight of Radium.** STEFAN MEYER (*Physikal. Zeitsch.*, 1913, 14, 124—125).—Hömgenschmid has verified his atomic-weight value, 225.97, found from the determinations for radium chloride by determinations for radium bromide, and, in common with Haschek, shown by spectro-

scopic tests that not more than 0.004% of barium can be present. Theoretical grounds can be adduced for the value 226. From magnetic deviation experiments and the value of the faraday, it can be deduced that the atomic mass of the  $\alpha$ -particle is 3.8 or 5% smaller than that of helium. Subtracting five times 3.8 from 226 gives 207.0, agreeing with the atomic weight of lead. This suggests an error in the determination of the atomic weight of helium, but the possibility is referred to that helium and the  $\alpha$ -particle may represent "non-separable" elements (Soddy). The value 3.8, however, makes the atomic weight of uranium 237.4 instead of 238.5, and until the complex ( $UI = UII + UX + UY$ ) has been further studied, arguments from the atomic weight of uranium are indefinite. There is no ground for doubting the value 226.0 for the atomic weight of radium or the purity of the International Standard (Mackwald, A., 1912, ii, 323). F. S.

**Revision of the Atomic Weight of Radium by Analysis of Radium Bromide.** OTTO HÖRIGESCHMID (*Monatsh.*, 1913, 34, 283-300).—The material which had given the value,  $Ra=225.53$ , by analysis of the chloride (A., 1912, ii, 523) was converted into bromide and fractionally crystallised thirty times. No change of atomic weight occurred during the process. Very full details are given of the analytical operations. Six analyses, with nearly a gram of radium bromide, in which the ratio  $RaBr_2/AgBr$  was determined gave the mean value  $Ra=225.96$ , with a mean variation in the separate experiments of 0.01, and a mean error of 1 in 40,000 of the weight of the radium bromide. Two analyses in which the ratio  $RaBr_2/Ag$  was found, gave in both cases  $Ra=225.97$ . The purest preparations of bromide did not show the barium line 4551.2, and were absolutely free from barium so far as spectroscopic test revealed. It is calculated that not more than 0.004% of barium could have been present.

The results of Whytlaw-Gray and Ramsay (A., 1912, ii, 413) are criticised in detail, and corrected for a constant error in the reduction of the weights to a vacuum. Their mean value recalculated should be 226.26, with a mean error of  $\pm 0.21$ .

Two determinations by their method, converting the bromide into the chloride by heating in hydrogen chloride, the second with nearly a gram of radium bromide, gave the value  $Ra=225.94$ .

It is estimated that the heat generated by the radium compounds may raise the atomic weight by 0.01. Seventeen analyses of radium chloride and bromide by two independent methods, in which the extreme values are included between 225.99 and 225.93, give the final value 225.97 ( $Ag=107.88$ ;  $Cl=35.457$ ;  $Br=79.916$ ). The mean departure from the mean is  $\pm 0.012$ . F. S.

**The Purity of the International Radium Standard.** EDUARD HASCHKE and OTTO HÖRIGESCHMID (*Monatsh.*, 1913, 34, 351-357).—By means of a large Rowland grating, radius of curvature 15 feet, with 72,000 lines at 20,000 to the inch, the spectrum in the neighbourhood of 4500 Å. units was examined of the purest radium bromide used in the atomic weight determinations (preceding

abstract), and of the mother liquors, in which all the impurities in the material, which was that employed in the atomic-weight determinations on the chloride (A., 1912, ii, 523), had been accumulated after twenty-five crystallisations of the bromide. A rod of electrolytic copper which was completely free from barium was used for the electrode. The rod was 7 mm. thick and provided with grooves, and one drop of the purest bromide solution containing 0.05 mg. of radium (metal) was tested with a powerful spark discharge. No trace of the barium line, 4554.24, was seen in the photograph. On a new electrode, a drop of a barium solution of strength 0.1% of the radium solution previously tested, showed this line faintly but clearly.

The mother liquors containing 75 mg. of radium bromide were tested as in the first case, a drop containing 0.25 mg. of radium (metal) being employed. The barium line was plainly visible. Addition of 0.1% barium increased the intensity of the line four times. If the original barium content of the mother liquors is taken as 0.03%, it follows that the original chloride, out of which the Austrian standards have been prepared, does not contain more than 0.001%, and the radium bromide used in the final atomic-weight estimations, not more than 0.002% of barium. This can make no appreciable difference in the values found. A similar degree of purity can be assumed for the International radium standard as for the Austrian standards, and for the barium to cause any error in the radioactive determinations, methods a hundred times more sensitive than the present must be employed.

F. S.

#### Heating Effect of Radium and its Emanation. ERNEST RUTHERFORD and H. ROBINSON (*Phil. Mag.*, 1913, [vi], 25, 312—330).

The heating effect of any  $\alpha$ -ray would not be a measure of the energy of the expelled  $\alpha$ -particle if the  $\alpha$ -particle lost energy before escaping from the atom. Experiment on the distribution of the heating effect among the emanation and its first three products were made to see if the observed emission of heat agreed with that calculated from the energy of the radiations expelled, and also to determine the heating effect of the  $\beta$  and  $\gamma$  rays. The relative calculated heating effects of the emanation, radium-A and -C, 28.8, 30.9, and 40.3, agree with the observed values, 29, 31, and 40%, but as the  $\beta$ -rays of radium-B are included in the results for radium-C, it follows that the percentage for this number should have been about 12.6 instead of 30.3. The difference is small, but it may prove to be significant. The heating effect of one curie of emanation and its products, in terms of the Vienna standard, is 1035 gram-calories per hour, when more than 9% of the energy of the  $\beta$ -rays is included. Under these conditions 99.2 calories are estimated to be due to  $\alpha$ -rays, 1.2 to  $\beta$  rays, and 0.1 to  $\gamma$ -rays. The total heating effect of 1 gram of radium is estimated to be 131.7 calories per hour, made up as follows: 25.1 due to  $\alpha$ -rays of radium-A, 28.6 to the  $\alpha$ -rays of the emanation, 30.5 to the  $\alpha$ -rays of radium-A, 30.1 to the  $\alpha$ -rays, 1.7 to the  $\beta$  rays, and 0.1 to the  $\gamma$ -rays of radium-B and -C.

F. S.

**Decomposition of Water by  $\alpha$ -Rays.** WILLIAM DUANE and OTTO SCHEUER (*Compt. rend.*, 1913, 156, 466—467\*).—A study of the decomposition of water in the solid, liquid, and gaseous state by  $\alpha$ -rays, care being taken to avoid excess of water, to have it in as thin a layer as possible, and to remove the gaseous products from the radiation as soon as formed. With ice at  $-183^{\circ}$ , hydrogen and oxygen are obtained in the proportion of 2:1 by volume. With water, the hydrogen is at first in excess, due to the formation of hydrogen peroxide, this in its turn being decomposed, and giving oxygen in excess. With water vapour, the hydrogen is largely in excess, and may amount to 50% of the total volume of gas liberated.

A radiation, capable of producing an ionisation current of one ampere in air, decomposes water, giving 0.1594 c.c. hydrogen and 0.0797 c.c. oxygen per second, these amounts being of the same order as those obtained by the electrolysis of water at  $15^{\circ}$ . W. G.

**The  $\beta$ -Rays of Radium-*B*, -*C*, -*D*, -*E*.** JEAN DANFÈS (*Le Radium*, 1913, 10, 4—6).—The experiments before carried out with thin-walled glass tubes of radium emanation (*A.*, 1912, ii, 219, 220) have been repeated with thin wires of silver and platinum made active in the emanation. There was no difference in the results, but the photographs with the glass tubes are much superior in sharpness. Tables are given of the character, value of  $H\rho$ , velocity, and energy of twenty-seven groups of  $\beta$ -rays from radium-*B* and -*C*, and of five groups from radium-*D* and -*E*. These results are corrected for slight retardation of the  $\beta$ -rays in passage through the walls of the tube. Some of the original photographs are reproduced.

F. S.

**The Penetrating Power of the  $\gamma$ -Rays of Radium-*C*.** ALEXANDER S. RUSSELL (*Proc. Roy. Soc.*, 1913, A, 88, 75—82).—Experiments were carried out with 300 millicuries of radium emanation in the attempt to detect the presence of a radiation more penetrating than the  $\gamma$ -rays of radium-*C* after passage through great thicknesses of mercury. With from 1 to 22.5 cm. of mercury the  $\gamma$ -rays are absorbed strictly according to an exponential law, and over this range are reduced in intensity from  $3.6 \times 10^9$  to 1. The value of  $\mu d$  is  $4.38 \times 10^{-2} (\text{cm.})^{-1}$ . This value is practically the same as that previously found for lead over the range from 2 to 22 cm., namely,  $4.37 \times 10^{-2}$  (*A.*, 1909, ii, 851). It is calculated that after passage through 28.5 cm. of mercury the  $\gamma$ -rays unabsorbed from 10 grams of radium would produce an effect less than 5 per cent. of the natural leak. If any ionising radiation exists more penetrating than the  $\gamma$ -rays, its intensity must be less than  $2 \times 10^{-6}$  of the initial  $\gamma$ -rays.

F. S.

**The Chemical Action of Penetrating Radium Rays. V. Influence of Penetrating Rays on Sterilised Aqueous Sucrose Solutions.** ANTON KILIAN (*Monatsh.*, 1913, 34, 359—364. Compare this vol., ii, 8).—Normal sucrose solutions were sterilised by long heating at  $100^{\circ}$ , and subjected to the action of the penetrating

\* and *L. Radium*, 1913, 10, 33—46.

rays of radium, in closed flasks in the absence of light, for several months, blank experiments without the radium being also performed. Formation of acid and a decrease in the rotation still took place in the solutions after sterilisation, although it is much smaller than in unsterilised solutions, rather less effect being produced after 2500 hours' exposure to the rays than formerly after 500 to 700 hours. The acid so produced must be relatively feebly dissociated, but its quantity is completely sufficient to account for the loss of rotatory power of the sucrose, through the inversion brought about by the hydrogen ion. The solutions, after exposure to the rays, reduce Fehling's solution, and the amount of invert sugar present, as so determined, agrees approximately with that calculated from the decrease of rotatory power.

F. S.

**Theory of the Concentration Variations in Radioactive Solutions.** EGON VON SCHWEIDLER (*Physikal. Zeitsch.*, 1913, 14, 198—200).—The mathematical theory of the von Schweidler variation in the emission of rays from a radioactive solution is considered in which the instantaneous concentration also undergoes a probability variation. Experimental complications, for example, when only a small part of the total radiation is for various causes observed by the observer, do not affect the general character of the results to be expected, as regards the relative magnitude of the variations and the law of distribution of the rays in time.

F. S.

**The Solubility of Radium Emanation in Water as Regards its Dependence on the Temperature.** MARTIN KOFLER (*Monatsh.*, 1913, 34, 389—400. Compare A., 1908, ii, 80).—The following results have been obtained, showing the variation of the solubility of radium emanation in water with temperature:

Temperature .....	0.5°	17.5°	35°	41°	51°	60°	74°	79°	82°	91°
Solubility .....	0.526	0.283	0.185	0.161	0.138	0.127	0.112	0.111	0.111	0.108

Both the solubility and the change of solubility with temperature decrease with increase of temperature. It is shown that the percentage change of solubility between 0° and 18° for a large number of gases increases with the molecular weight of the gas. It is 7% for helium, 33% for argon, and 49% for the radium emanation. Above 70° the solubility changes so little that it may be considered practically constant, but no evidence of a minimum solubility, as in the case of hydrogen and helium, was obtained. The solubility of gases generally is discussed.

F. S.

**A Relation between Ionisation by Cathode Rays and Certain Chemical Effects.** E. JACOT (*Phil. Mag.*, 1913, [vi], 25, 215—234).—The investigation is concerned with the proportion of the chemical action of the cathode rays due (1) to direct action, as supposed by Schmidt (A., 1902, ii, 237), of the negative charge neutralising the positively charged ion and causing chemical dissociation (2) to thermal effects, (3) to the secondary action of the

gases in the tube. In the case of yellow phosphorus, the rapid transformation into the red variety is attended by rapid exhaustion of the nitrogen in the tube. The mass of phosphorus so transformed exceeds the amount that could be formed as a direct thermal effect, assuming the energy of the cathode rays to be quantitatively converted into heat, and when the phosphorus is screened from direct impact of the rays the transformation attended by absorption of gas still goes on. The absorption is proportional to the equilibrium ionisation of the nitrogen. The ionisation is inversely proportional to the kinetic energy of the cathode rays for a range of velocities from 2.92 to 4.76 ( $\times 10^9$  cm./sec.), and varies linearly with the pressure from 0.083 to 0.025 mm. But the total number of active atoms or molecules in the gas is of a much higher order than the number of ions. Most probably the absorption is not due to the ions, but to an atomising effect of the rays, the active agent being monatomic nitrogen, and the number of such molecules being proportional to the ionisation of the gas. F. S.

**Positive Ionisation Produced by Platinum and by Certain Salts when Heated.** FRANK HORTON (*Proc. Roy. Soc.*, 1913, A, 88, 117—146. Compare A., 1910, ii, 176).—The thermionic currents, resulting from the emission of positive ions by heated platinum, aluminium phosphate, sodium phosphate, and sodium pyrophosphate, have been investigated at 1080° and 1190°.

In the case of platinum and pure aluminium phosphate, the initial thermionic emission decreases very rapidly with time, and after a few hours becomes extremely small. With sodium phosphate the emission increases at first, this stage being followed by one in which the effect slowly decreases, but even after many hours' heating a very considerable thermionic current is obtained with this substance.

The view is put forward that the positive ionisation exhibited by platinum (and by metals generally) is largely due to the emission of absorbed gases, but that in the case of sodium phosphate a considerable part of the effect is due to the emission of positively charged sodium atoms. This view is discussed in reference to the observations of other workers on the ionic emissive power of heated substances. H. M. D.

**Ionisation Produced by Heated Salts.** CHARLES SHEARD (*Phil. Mag.*, 1913, [vi], 25, 370—389).—An examination has been made of the ions which are emitted by cadmium iodide when this substance is heated out of contact with metal. The observations show that both positive and negative ions are emitted by the salt under these circumstances. The initial emission consists almost exclusively of negative ions, but when the temperature is maintained for some time at 350° to 500° the positive ionisation increases, reaches a maximum, and then gradually diminishes; the negative ionisation, on the other hand, falls away continuously. In addition to the emission of ions from the heated salt, it is found that the observed ionisation must be partly due to ionisation of

the vapour. This may arise from the action of the vapour on the electrodes, or it may be a volume ionisation, or possibly is a combination of the two effects. The distilled salt is less active than the undistilled, and successive distillations are found to exhibit alternations in their power of emitting positive and negative ions. These distillations, which give rise to a comparatively large negative thermionic current, exhibit a small positive emission and vice versa. The fact that continued distillation leads to a diminution in the percentage of iodine in the substance, and that iodine itself exhibits ionisation effects of a similar kind seems to show that the negative ionisation observed with cadmium iodide is largely due to the negative constituent.

H. M. D.

**Separation of Corpuscles in Chemical Reactions.** SERGIAN M. TANATAR and E. BURKSE (J. Russ. Phys. Chem. Soc., 1913, 45, 1-6).—Immersion of a charged conductor connected with an electroscope into the gas evolved during the catalytic decomposition of hydrogen peroxide by platinum-black shows the gas to be strongly ionised. A thin aluminium plate placed under the base of the glass vessel retards the loss of charge. Similar experiments were also made on the oxidation of sodium sulphite or arsenic trioxide by hydrogen peroxide solution.

The results do not allow of any definite statement concerning the cause of the ionisation observed.

T. H. P.

**A New Method for Concentrating Polonium.** FRITZ PASCH (Monatsh., 1913, 34, 401-402). Pure polonium, formed from radio-lead, may be obtained as well by the electrolysis of lead nitrate as lead acetate solution, when the voltage and acid concentration are such that lead is no longer deposited on the cathode. Polonium diffuses either not at all or only in extremely minute amount through animal bladders or parchment paper, and may be separated from lead and radio-lead by this method. By dialysing a solution of radio-lead through thin parchment paper it may be obtained practically free from polonium, which remains behind in the cell.

F. S.

**Solubility of the Active Deposit of Thorium in Various Solvents.** CHARLES FREDERICK HOGLEY (Phil. Mag., 1913, [vi] 25, 331-332).—Water, solutions of salts, hydroxides, and acids always dissolve thorium-B in relatively larger amount than thorium-C, especially in the case of short treatments. Boiling water for fifteen minutes dissolves about 35%, and for an hour 70%; potassium iodide solution dissolves the deposit about twice as fast as water; dilute acids dissolve it much more rapidly. Organic solvents dissolve it at the same rate as water, but thorium-C is dissolved more easily than thorium-B, the latter being insoluble in carbon disulphide and methylene iodide, which dissolved some 20% of the thorium-C in ten minutes. Benzene, bromoform, etc., behaved very similarly, but the thorium-B was slightly soluble.

F. S.



**The Chemical Properties and Relative Activities of the Radio-products of Thorium.** HERBERT N. MCCOY and CHARLES H. VIOL (*Phil. Mag.*, 1913, [vi], 25, 333-359).—The results of experiments on the chemical nature of the various thorium products agree with the known behaviour of these substances. Mesothorium-II is separated from thorium by hydrogen peroxide at 60° or 70°, and is left in the solution. It is carried down by a precipitate of barium sulphate in slightly acid solution. In absence of thorium, radiothorium is partly precipitated with barium sulphate in acid solution, up to 50%, and to about 5% by mercuric or lead sulphide. Very numerous other reactions are given confirming previous knowledge.

A comparison of the  $\alpha$ -activities of thorium-B, -C, and -D with that of thorium-X, emanation and -A, gave the ratio of the first to the second as 0.427. The products of radiothorium are 5.23 times as active as radiothorium itself. A redetermination of the range of the  $\alpha$ -particles of thorium-X gave the value 4.1 cm. (of air at 0° and 76 cm.), instead of 5.7 cm. as previously found. The new value agrees with what is to be expected from the period of the substance. The values found for the activities of the various groups of products are in excellent agreement with the theoretical law that the total ionisation produced by an  $\alpha$ -particle is proportional to the two-thirds power of its range. The following is the distribution of the  $\alpha$ -activity among the separate products: Th, 11.4%; Ra-Th, 14.4%; Th-X, 15.5%; Th Em., 17.6%; Th-A, 18.6%; Th-C, 22.5%, as calculated from this relation, and in agreement with the determined values.

F. S.

**Tables of Radioactive Constants.** LÉON KOLOWRAT (*La Radiac.*, 1913, 10, 1-4).—These tables are similar to those published in former years, and give the present knowledge with regard to the radio-elements, their periods, and radiations, together with particulars of the physical constants of the latter, and some other data relative to radioactivity.

F. S.

**Periodic System and Radio-elements.** ALEXANDER S. RUSSELL (*Chem. News*, 1913, 107, 49-52).—The known rule as regards the change of family in the Periodic Table of an element undergoing an  $\alpha$ -ray change is modified and supplemented by a similar rule with regard to the  $\beta$ -ray changes. (1) The  $\alpha$ -ray change results in a product belonging to a family the number of which is either two units greater or two units less than that of the parent. (2) The  $\beta$ -ray change or rayless change results in a product the number of which is either one unit greater or one unit less than that of the parent. Tables are given showing how well these rules are obeyed in the three series. Branch products are not considered. Uranium-X is put intermediate between uranium-I and -II, and a new member, uranium-X<sub>2</sub>, in group V.I of the table is predicted. The recent results for radioactinium (Russell and Chadwick, *Nature*, Dec. 26th, 1912) are discussed. Radioactinium-II, a new member giving  $\alpha$ - and  $\beta$ -rays, is placed in group V.A, and its product, actinium-X, in group II.A. The rules were obtained independently

of, and are supported by, Fleck's results on the chemical nature of the  $B$ -members, the  $C$ -members, radium- $E$ , and mesothorium- $II$  (see T., 1913, 103, 381). F. S.

**Radio-elements and the Periodic Law.** FREDERICK SODDY (*Chem. News*, 1913, 107, 97—99\*).—The known disintegration series, many of the members of which have recently been shown by Fleck to be non-separable from other elements (T., 1913, 103, 381), agree with the author's  $\alpha$ -ray change rule and the corollary with regard to the  $\beta$ -ray change (Russell, preceding abstract). The expulsion of the  $\alpha$ -ray lowers the number of the group in the Periodic Table to which the radio-element belongs by two, and the expulsion of the  $\beta$ -ray increases the number of the group by one. This holds throughout the disintegrations, including the branch series which commence at the  $C$ -members. The emanations in the zero group, which expel  $\alpha$ -rays, furnish short-lived  $A$ -members, which it is predicted are in the  $VIB$  group in the place already occupied by polonium. Fleck's results (*loc. cit.*) are in accord with the rules, and for the members the chemical nature of which cannot be directly determined, owing to too short period of existence, it is predicted that the  $A$ -members and the  $C$ -members are in group  $VIB$ , and will be non-separable from polonium, whilst thorium- $D$ , actinium- $D$ , and the corresponding member in the radium series, radium- $C_2$ , are in the  $IIIB$  group, and should be non-separable from thallium. Whenever a radio-element falls in a place in a Periodic table occupied by another, it is chemically identical with, and non-separable from, that element, independently of the atomic weight of the radio-element and of the series in which it originates; thus, occupying the place in the  $IV.A$  group already occupied by thorium, are ionium, radiothorium, radioactinium, and uranium- $X$ , a group the members of which vary in atomic weight by about 6 units. The unknown product of uranium- $X$  (group  $IV.A$ ) by a  $\beta$ -ray change is called "eka-tantalum," and occupies a vacant place in the table in the group  $VA$ , the heaviest member of the family known being tantalum. It should prove to be separable from tantalum. Actinium should also be separable from lanthanum. All the members expelling  $\alpha$ -rays occupy even numbered groups, except the  $C$ -members in group  $VB$ , non-separable from bismuth. These disintegrate dually, in one mode a  $\beta$ -ray change preceding, and in the other mode following an  $\alpha$ -ray change. It is suggested that eka-tantalum may disintegrate similarly, in one mode a rayless change producing uranium- $II$  (group  $VI.B$ ), and in the other an  $\alpha$ -ray change producing actinium (group  $IIIA$ ). Evidence is given of an excessively minute growth of actinium over a term of years from the old preparations of uranium- $X$  separated in 1909 from 50 kilograms of uranyl nitrate.

The six end-products all occupy the place in group  $IVB$  occupied by lead, and the atomic weight of lead, 207.1, is intermediate between the calculated atomic weights 206.0 and 208.5 of the main end-products of the uranium radium and the thorium disintegra-

\* and *Jahrb. Radioaktiv. u. Elektrochem.*, 1913, 10, 18—197.

tion series. These end-products should be non-separable from lead, and lead may be a mixture of these end-products.

In the case of thorium and ionium the two elements possess, so far as can be seen, identical spectra. A chart is given showing graphically the passage of the radio-elements from place to place through the Periodic Table.

The prediction with regard to the non-separability of thorium *D* and thallium has since been confirmed by Fleck, who finds that thorium *D* can be quantitatively separated from the *B*- and *C*-members by precipitating in the solution potassium by means of platinum chloride.

F. S.

**The Position of the Radio-elements in the Periodic System.** KASIMIR FAJANS (*Physikal. Zeitsch.*, 1913, 14, 136—142\*).—Soddy's  $\alpha$ -ray change rule, that the position of the radio-element changes into the next group but one from right to left in the horizontal row of the periodic system, is shown to be general. In the same way the  $\beta$ -ray change in general causes a change of one from left to right in the system. By the aid of these rules all the radio-elements can be placed without uncertainty in the Periodic Table. In all properties the disposition of the elements so obtained corresponds with what is to be expected for the members of the last two horizontal rows of the periodic table, which shows that these two rows are the expression of the law of change of the elements.

The only difficulty in the application of the  $\alpha$ -ray rule is in the change of the alkaline-earth elements, as radium, into the emanations, which occurs with expulsion of both  $\alpha$ - and  $\beta$ -rays. From the rules, mesothorium-II is placed in the third group, and radium-B in the fifth. The short-lived *C*-members come into the sixth group. The change from radium-A to lead is written VI, IV, V, VI, IV, V, VI, IV, which is analogous to the change of uranium-I into ionium, VI, IV, V(?), VI, IV. The unknown fifth group member is regarded as a short-lived element intermediate between uranium-X and uranium-II, which is supported by the fact that uranium-X gives two types of  $\beta$ -rays, one very hard, such as would be given by a short-lived element. The members Ra-C<sub>2</sub>, Th-D, and Ac-D are placed in the third group with thallium.

The remarkable fact shown by the table so constructed is that places which elsewhere in the Periodic Table contain only one element here contain several, in some cases six. All the elements of one group, with atomic weights differing from one another by two units, are so completely similar that it has not been possible to separate them by chemical or crystallisation methods, and a mixture of such elements, separated from a mineral, behaves chemically as one element. The atomic weight found for such a complex element would be nearest to that member with the longest period of life, and therefore present in the greatest quantity. It is suggested that thallium is formed in an  $\alpha$ -ray change from bismuth, itself regarded as the product of "thorium-D," in a  $\beta$  ray change.

The discrepancy between the atomic weight of lead, 207.1, and that of the end-product of the uranium series, 206.5, would be

\* and *Le Radium*, 1913, 10, 61-65.

explained if common lead were a mixture of the latter and "thorium- $D_2$ ," which is the product of thorium- $C'$ , and must be very similar to lead.

The question of the origin of actinium is discussed, and two possible alternatives are considered. The results throw much new light on many questions arising out of the Periodic Law. F. S.

**Radioactive Changes and the Periodic System of the Elements.** KASIMIR FAJANS (*Ber.*, 1913, 46, 422).—The paper contains a fuller account of the author's views (preceding abstract). It is probable that what holds good among the radio-elements applies also in other parts of the Periodic Table, and that elements there may also be mixtures of unseparable groups of elements. The position of the rare-earth elements in the Periodic Table is discussed at length. It is supposed that these elements may be in process of continuous change with loss of hydrogen, nebulium, or proto-fluorine atoms rather than of helium. Tantalum appears as the parent of the rare-earth group and columbium of yttrium. The anomalies in the Periodic Table, such as tellurium and iodine, are also referred to. F. S.

**Some Relations between the Radio-elements giving  $\alpha$ -Rays.** RICHARD SWINNE (*Physikal. Zeitsch.*, 1913, 14, 112—145).—The experimental values for the velocity of the  $\alpha$ -particles found by Geiger and Nuttall are compared with the values calculated from the periods of the elements producing them according to the three relations proposed by Geiger and Nuttall, Swinne and Wilson, and it is shown that all three formulae show nearly equally good agreement with the observed values. From the author's formula it can be deduced that the difference between the initial velocity of the  $\alpha$ -ray member of one series and that of the analogous member in another series is approximately constant for the two series. Expressing this difference as  $\Delta v_\alpha$  for the radium and thorium, and  $\Delta v_a$  for the radium and actinium series respectively, the values of these two constants are 0.13 and  $-0.20$  ( $\times 10^9$  cm. sec.). The calculated value for the velocity of the  $\alpha$ -ray of the unknown  $C'$ -member of actinium is 2.27.

The disintegration constants of analogous  $\alpha$ -ray-giving members of different series stand in constant ratio to one another. The logarithm of this ratio between the radium and actinium series is  $1.3 \times 10^{-5}$  and between the radium and the thorium series  $4.8 \times 10^{-5}$ . F. S.

**A Relation between the Kind of Radioactive Change and the Electrochemical Behaviour of the Resulting Radio-element.** KASIMIR FAJANS (*Physikal. Zeitsch.*, 1913, 14, 131—136).—Two rules are proposed, and shown to be followed in all cases where they can be tested:

(1) An  $\alpha$  ray change gives a product more electropositive than the parent substance.

\* and *Le Radium*, 1913, 10, 57—60.

(2) A  $\beta$ -ray change gives a product more electronegative than the parent substance.

The rule with regard to the  $\beta$ -ray change is considered to apply also to rayless changes, and  $\beta$ -rays of very low velocity, not yet detected, may be supposed to be emitted in these cases also. The three disintegration series are discussed in detail in so far as there is evidence of the electrochemical character of the members.

It is assumed that uranium-X is intermediate between uranium I and -II, which then conform to the rules. The change of radium and of thorium-X, in which both  $\alpha$ - and  $\beta$ -rays are emitted, is supposed to be complex, an alkali-metal first resulting as the product of the  $\alpha$ -ray change, which then in a subsequent  $\beta$ -change suffers transformation into the much more "noble" emanations. It is predicted that radium C' should be nobler than radium C or -D. Such simple relations, the change in the character of the atom being analogous to electrochemical changes, are very unexpected, for it has always been considered that these atomic changes are concerned with regions of the atomic structure quite different to those conditioning chemical changes.

F. S.

The Radioactivity of the Mineral Springs of Tyrol. IV. MAX HAMBERGER and KARL KETSE (*Monatsh.*, 1913, **34**, 403-423. Compare A., 1911, ii, 1049).—Tables are given of the amount of radium emanation of numerous Tyrolean springs in Mache units, together with particulars of the locality, the kind of rock in which the spring occurs, and its temperature.

R. GRENGG contributes the results of a petrographic study of the rocks. The decay curves of the active deposit from the iron spring of Bad Ratzes and the strongly active potable water of Schreiberhof in Tscherns are shown, and are in agreement with that due to radium.

F. S.

Electrical and Chemical Effects of the Explosion of Azoinide. PAUL J. KIRKBY and JAMES E. MARSH (*Proc. Roy. Soc.*, 1913, **A**, **88**, 90-99).—Measurements have been made of the quantity of electricity which is set free when azoinide is exploded by the passage of an electric spark through the vapour contained in a vessel provided with electrodes which were connected in series with a ballistic galvanometer and a potential difference of about 100 volts. The galvanometer readings show that the number of ions set free is exceedingly small in comparison with the number of molecules decomposed in the explosion. The ratio was always less than 1 to 100,000, and this seems to indicate that dissociated atoms do not in general carry electrostatic charges. It is supposed that the formation of the ions is due to those impacts between the dissociated atoms which occur under specially favourable conditions, amongst which a relatively high velocity is probably the most important. Except under these circumstances, the combination of the dissociated atoms takes place without the production of ions.

From experiments at different pressures it was found that the azoinide could not be exploded when the pressure was less than

about 10 mm. In the case of pure azoimide this limiting pressure would probably be smaller. The value of the limiting pressure is much smaller than that obtained in previous experiments with electrolytic gas, for which 80 mm. was observed as the lower limit.

In drying the gas it was observed that azoimide is very readily absorbed by phosphoric acid, although no change in volume occurs when fresh phosphoric oxide is employed as drying agent. After the explosion experiments, copper azoimide was found to be present in the gold-plated brass explosion vessel, and it is shown that this is probably formed in the actual explosion, the dissociated  $N_2$ -group being driven through the layer of gold into the brass as a consequence of the forces developed in the molecular disruption.

H. M. D.

**Duration of Luminosity of Electric Discharge in Gases and Vapours.** (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1913, *A*, 88, 110—117).—Some experiments are described, which show that the luminosity accompanying the electrical discharge persists for an appreciable period after the cessation of the discharge. This is not only the case for discharge through vapours of metals and non-metals, but can be observed when the discharge takes place through gases such as hydrogen, oxygen, carbon dioxide, and air between non-volatile electrodes. The luminosity gradually fades away when the discharge ceases, but there is no immediate alteration in the spectrum, although a change may sometimes be observed in the later stages in consequence of a difference in the rate of decay of the lines. The effects in question, the duration of which is less than one-thousandth of a second, are quite distinct from the after-glow effects in nitrogen and in gaseous mixtures containing oxygen or hydrogen.

H. M. D.

**Electrical Discharge in Helium and Neon.** HERBERT E. WATSON (*Proc. Camb. Phil. Soc.*, 1913, 17, 80—107).—Measurements have been made of the sparking potentials in pure helium and neon at different pressures, the discharge taking place between plane aluminium electrodes, 15 mm. apart. The minimum spark potential was found to be 184 volts for helium and 200 volts for neon, the pressures corresponding with these minima being 2.4 and 2.8 mm. respectively. For pressures greater than 10 mm. the relation between the spark potential and the pressure is represented graphically by a straight line, the increase in the potential being 30 volts per cm. pressure in the case of helium and 22 volts per cm. for neon.

With a cathode of sodium-potassium alloy the minimum spark potential in neon is near to and not greater than 145 volts, and the cathode fall amounts to 85 volts. With aluminium electrodes which have been run for a sufficiently long time, the cathode fall is at most 164 volts for helium and 170 volts for neon. The cathode fall in neon with cathodes of copper, carbon, magnesium, and calcium is approximately 221, 217, 150, and 150 volts respectively.

The electrodes have been found to exhibit marked fatigue effects,

and these appear to be of two kinds, one representing a true fatigue and the other a reluctance to allow the current to start for a second time when one discharge has already taken place.

In view of the brilliancy of the discharge through pure neon, some measurements were made of the efficiency of the negative glow, but the data showed that the actual intensity of the light was much smaller than the estimated intensity. At pressures between 10 and 16 mm. the efficiency was raised to about 4 watts per candle by making use of a sodium-potassium electrode.

The light emitted by both helium and neon under the influence of the discharge produces very marked physiological effects. When, for instance, the light from a tube of about 0.1 candle power was allowed to fall on the unprotected eyes for about fifteen seconds, it gave rise to a violent headache, followed by temporary blindness. On this account it was necessary to wear dark brown glasses during the whole of the experiments. Similar effects have been noticed with argon, krypton, and xenon, and it is suggested that the phenomenon may be connected with the fact that the spectra of these elements contain a comparatively small number of intensely bright lines.

H. M. D.

**The Hall Effect.** JOHANNES KOENIGSBERGER and G. GOTTFELD (*Physikal. Zetsch.*, 1913, 14, 232-237).—Evidence is brought forward to show that the Hall effect can be accounted for on the basis of the electron theory. By reference to the data for graphite, molybdenite, and a silicon-iron alloy (containing 5.2% of iron), it is shown that the Hall effect changes with temperature to about the same extent as the number of electrons. It is further found that the ratio of the Hall effect to the specific resistance is of the same order of magnitude for metalloids, metals, and alloys, although the two quantities vary to the extent of 1 to  $1.10^7$  when the extreme members of the composite group are compared. The behaviour of alloys, such as German silver and constantan, suggests that the low conductivity which they exhibit is not due to the smallness of the free path or the energy of the electrons, but to the presence of a very small number of electrons.

H. M. D.

**The Changes in the Electrical Resistance of Wires which have been Drawn and Subjected to Torsion, and also of Drawn and Twisted Wires on Warming: Gold, Silver, Copper, Nickel, and Iron.** FRITZ CRENNER (*Zetsch. physikal. Chem.*, 1913, 82, 457-503).—The paper commences with a critical résumé of the work which has been done on this subject. The experimental part of the paper consists in an account of the changes in the resistance of wires which have been warmed to definite temperatures for measured periods of time. It is shown: (1) That the resistance of drawn wires of gold, silver, and copper falls at a constant temperature, and the rate of decrease is more rapid the higher the temperature. After a time the resistance reaches a constant minimum; on further increasing the temperature after the minimum has been reached, an increase in the resistance takes

place; for gold the increase commences at  $300^{\circ}$ , and for silver and copper at  $400^{\circ}$ . (2) On successively warming drawn wires for periods of three minutes and measuring the cold wires, it is shown that a minimum specific resistance is obtained at a definite temperature, and that this minimum specific resistance is independent of the cross-section of the wire. For gold the minimum is found at  $181^{\circ}$ ; silver,  $480^{\circ}$ ; and copper,  $450^{\circ}$ . The temperature at which the minimum occurs is the same as that at which the coarse recrystallisation of the crystallite begins, and so is the same as the temperature at which small crevices begin to be formed in the wires, which naturally cause an increase in the resistance. In the case of nickel the minimum value of the specific resistance is obtained at  $550^{\circ}$ , and remains constant whilst the temperature is raised  $300^{\circ}$ . The minimum for iron wires is found at  $600^{\circ}$ , and this increases on increasing the temperature due to chemical changes in the substance of the wire. (3) Laminae are produced on drawing a wire due to a movement of parallel crystallite surfaces, and at the same time an increase in the resistance is brought about. On warming such drawn wires to the temperature of the minimum resistance, the laminae are destroyed and replaced by an irregular, crystallite mass, and the resistance falls to its original value before drawing. (4) On bending or subjecting a wire to a strong torsion the resistance of a wire is increased, due to the formation of small crevices; this increased resistance is not changed by warming. (5) On lowering the temperature, the resistance, in the direction of the axis of a wire made up of laminae, decreases more quickly than the resistance in the direction at  $90^{\circ}$  to the axis. (6) The greater specific resistance of drawn wires is due to the orienting laminae lying in the direction of their poorest conductivity, and is apparently uninfluenced by the loosening of the crystals. (7) Permanent changes in the resistance only occur when there is a definite change in the crystal structure. The hypothesis that on working metals a new phase appears is shown to be incorrect.

J. F. S.

**The Theory of Electrolytic Ions. VI. The Conductivity of Pure Water.** RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1913, 82, 612—620. See A., 1912, ii, 323 and also *Festschrift W. Nernst*, 1912, 276).—The author calculates the mobilities of the hydrogen and hydroxyl ions at various temperatures from molecular kinetic considerations; the values obtained are compared with those obtained from the Kohlrausch measurements. It is shown that in every case the Kohlrausch value is much larger than the calculated value, in many cases the Kohlrausch value being more than four times as large as the calculated. A theory of the migration of ions, resembling the Grotthius theory, is then considered. In this case the passage of an ion is supposed to be partly due to its own actual motion and partly due to colliding with an undissociated molecule with which it combines and sets free the corresponding ion of the undissociated molecule. In this way part of the distance, proportional to the number and diameter of the undissociated molecules lying in the path, is covered at an extremely high velocity, thus making



the apparent velocity much larger than that calculated on the molecular kinetic hypothesis. On comparing the values obtained in this way with the experimental results, the former are found to be somewhat larger than the latter. Hypotheses are considered which would slightly reduce the calculated values. J. F. S.

**Conductivity, Dissociation, and Temperature-coefficients of Conductivity of Certain Inorganic Salts in Aqueous Solution, as Conditioned by Temperature, Dilution, Hydration, and Hydrolysis.** E. J. SHAEFFER and HARRY C. JONES (*Amer. Chem. J.*, 1913, 49, 207—253. Compare Hosford and Jones, A., 1911, ii, 960; Winston and Jones, A., 1911, ii, 961; Howard and Jones, this vol., ii, 11).—In continuation of earlier work, conductivity measurements have been made at temperatures between 0° and 65° of ammonium hydrogen sulphate, tetraethylammonium iodide, ammonium sodium hydrogen phosphate, sodium chloride, chlorate, and perchlorate, disodium hydrogen phosphate, potassium chlorate, perchlorate, and phosphate, calcium chloride, strontium chloride, barium bromide and formate, magnesium chloride and sulphate, manganous chloride and nitrate, aluminium chloride, nitrate, and sulphate, the violet forms of chromic chloride, nitrate, and sulphate, lead nitrate, nickel nitrate, copper ammonium sulphate, and uranyl sulphate.

The results confirm the more important relations established by the earlier work. The dissociation was found to decrease with rise of temperature in all cases except that of potassium phosphate.

It has been found that the hydrolysis of chromium salts increases rapidly with rise of temperature, and that the hydrolytic products only slowly recombine as the solution cools. It follows, therefore, that in purifying a chromic salt for conductivity experiments, it must not be heated to a higher temperature than that at which the conductivity is to be determined, since the dehydrolysis time factor persists for months. This precaution does not appear to be necessary in the case of other salts.

It is shown that considerable error may be introduced into conductivity measurements unless the proper water corrections are applied. The purity of the air in the room must be the same when the water-cell is filled as when the solutions are prepared. Care should also be taken to ensure that the air is as free from impurities as possible.

The influence of hydration, hydrolysis, and polymerisation in conductivity determinations is discussed, and it is pointed out that the Kohlrausch method is not suitable for measuring the dissociation of highly polymerised sulphates or for determining the dissociation of any electrolyte which is both hydrated and hydrolysed.

E. G.

**Citrophosphate Solutions. II. Electrical Conductivity of Aqueous Solutions of Citric Acid and Phosphoric Acid.** UGO PRATOLOGO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 86—89. Compare A., 1911, ii, 865).—The paper records the results of con-

ductivity measurements of binary mixtures of citric acid with phosphoric acid, arsenic acid, and hydrochloric acid in aqueous solution. The curves present no abnormality, and therefore show no evidence of the existence of complex ions. R. V. S.

**Electrical Conductance of Non-aqueous Solutions.** LEON FRAWIN SHAW (*J. Physical Chem.*, 1913, 17, 162—176).—The conductivities of mercuric chloride, iodine, and lithium chloride in acetone, and of mercuric chloride and iodine in epichlorohydrin were compared with the dielectric constants of the purified solvents. The molecular conductivity of lithium chloride in acetone first increases, then decreases, and finally increases again on dilution. None of the solutions examined approached a constant molecular conductivity at infinite dilution, so that the "degree of dissociation" could not be calculated.

The dielectric constants of acetone and epichlorohydrin, according to Walden, are 21.0 and 26.0 respectively. Neglecting the question of ionic mobility, mercuric chloride is in accord with Nernst's hypothesis in having a higher conductivity in epichlorohydrin than in acetone, but iodine, on the contrary, has a much higher conductivity in acetone. The author did not make any measurements of dielectric capacity, but it is to be noted that his solvents by the conductivity test were somewhat purer than Walden's.

Solutions of a number of metallic chlorides, iodides, etc., in ten organic solvents of various types were examined qualitatively. No relationship appears to exist between the dissociating power of a solvent and its dielectric constant, degree of association, or residual affinity. R. J. C.

**Abnormal Electrical Conductivity Changes. IV.** ALEXANDER NICOLAEVITSCH SACHANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 102—136. Compare A., 1912, ii, 422, 730).—Theoretical considerations, together with the results obtained on investigating the conductivity and viscosity changes of solutions in aniline, acetic acid, etc., with dilution, lead to the following conclusions.

The molecular conductivity increases with dilution in the more concentrated solutions, and later diminishes continuously with dilution; the maximum value is reached at a dilution corresponding with  $x = (m-2)/(2m-2)$ ,  $m$  being the number of molecules of dissolved salt in the complex,  $mC.pB$  (see A., 1911, ii, 689), and  $x$  the number of polymerised molecules. The rate of diminution occurring on dilution increases with  $m$ , that is, with the complexity of the group conducting the current.

This appearance of a maximum conductivity in concentrated solutions is regularly met with in cases of abnormal conductivity changes. The formation of a minimum molecular conductivity with increasing dilution is also a regular phenomenon, increase of dilution beyond the point of minimum conductivity being accompanied by normal increase of the latter.

It is shown that cases of masked abnormality in the change of

molecular conductivity on dilution may occur when either the concentration of the polymerised molecules is not high, at any rate for low dilutions, or the degree of electrolytic dissociation of these molecules is not considerably higher than that of the simple molecules. Those cases must also be termed abnormal in which  $d\mu/dr$  has a positive value (the molecular conductivity increasing with the dilution) and  $d^2\mu/dr^2$  changes its negative sign at a certain dilution. Masked anomalies may also give rise to a fold in the molecular conductivity-dilution curve,  $d\mu/dv$  assuming the value zero, although positive for all neighbouring dilutions.

T. H. P.

**The Addition of Alkyl Halogens to Thiocarbamides.** HEINRICH GOLDSCHMIDT and HANS KRF. GUNZ (*Zeitsch. Elektrochem.*, 1913, **19**, 226—234).—The electroconductivity of allylthiocarbamide ethiodide,  $C_3H_5\cdot NH\cdot CS\cdot NH_2EtI$ , is determined in aqueous solution at 25°. It is shown that this substance is not hydrolysed in aqueous solution, and has a value  $\lambda_{\infty} = 102.2$ . From this value the migration velocity of the cation,  $C_3H_5\cdot NH\cdot CS\cdot NH_2Et$ , is calculated as 25.9. The electroconductivity is also determined in absolute alcohol, and in alcohol containing water; the water concentrations measured are 0.02*N*, 1.0*N*, 2.0*N*, and 10.0*N*. It is shown that small additions of water do not effect the conductivity; the 2.0*N*-water-alcohol solution shows an increase, which is comparatively small, whilst in the case of the 10.0*N*-solution there is a great increase. In the very dilute solutions of the salt it is shown that in all cases the conductivity is approximately the same. The change in the conductivity is shown to be due to an increased ionisation, and not to a change in the migration velocities of the ions. The equivalent conductivity of a number of thiocarbamide derivatives was determined in absolute alcohol and in alcohol containing 0.02*N*-water. The following values for  $\lambda_{\infty}$  in absolute alcohol were obtained. Allylthiocarbamide ethiodide,  $\lambda_{\infty} = 43.8$ ; ethobromide,  $\lambda_{\infty} = 41.5$ ; methiodide,  $\lambda_{1024} = 38.63$ . Phenylthiocarbamide ethiodide,  $\lambda_{1024} = 39.26$  in 0.02*N*-water-alcohol; ethobromide,  $\lambda_{1250} = 37.19$  in 0.02*N*-water-alcohol; methiodide,  $\lambda_{1250} = 37.83$  in 0.02*N*-water-alcohol. Thiocarbamide methiodide,  $\lambda_{\infty} = 48$  in absolute alcohol. The velocity of combination of the various thiocarbamides with alkyl haloids was determined by measuring the conductivity in water-alcohol solutions at measured intervals of time, and so determining the amount formed from curves obtained in the above-mentioned conductivity determinations. Allylthiocarbamide reacts with ethyl and methyl iodides at approximately the same rate; diphenylthiocarbamide reacts with methyl iodide much more slowly. The addition of water to the alcohol solutions makes only a small difference in the velocity constant; up to 2.0*N*-water there is no appreciable change in the velocity constant, but with a 10*N*-water-alcohol solution in the formation of allylthiocarbamide ethiodide the constant increased from 0.253 to 0.296. The slight influence of water on the velocity of reaction is remarkable in view of its great influence on hydrolysis in non-aqueous solutions. J. F. S.

**The Reduction to Hydrogen Peroxide of Oxygen Dissolved under Pressure.** FRANZ FISCHER and OTTO PRIESS (*Ber.*, 1913, **46**, 698-709).—The authors have confirmed the experiments of Moritz Traube with respect to the formation of hydrogen peroxide at the cathode when air is led through the catholyte. When the air is replaced by oxygen at atmospheric pressure, a 0.32% solution of hydrogen peroxide is obtained, as against a 0.26% with air, the current density being 0.02 ampere per square dm. The effect of various conditions on the yield was studied in detail. The current yield is diminished by rise in temperature, and increased by vigorous stirring. The best electrolytes are sulphuric acid (0.1%) and phosphoric acid; boric acid may also be used. Solutions of neutral salts are not suitable, owing to the formation of alkali at the cathode, unless an insoluble derivative of hydrogen peroxide is formed, as, for example, calcium hydroperoxide from an ammoniacal solution of calcium chloride. The best electrode material is mercury; when, however, the catholyte is stirred, mercury goes into solution, so that all the experiments were made with amalgamated gold electrodes. The current yield diminishes with time, and the concentration of the hydrogen peroxide increases to a maximum and then falls, owing to the reduction of the hydrogen peroxide formed. The current-yield increases with diminution in current density.

A special steel apparatus was constructed, which permitted electrolyses in a divided cell being carried out under pressures up to 100 atmos., the catholyte being stirred by means of an electromagnetic attachment.

Under high oxygen pressures the current yield and concentration of hydrogen peroxide increase with the pressure, the voltage necessary diminishing at the same time. At 100 atmos. pressure and a current density of 2 amperes per sq. dm., using 2 volts, 2.7% solutions of hydrogen peroxide can be obtained, that is, 390-400 grams of hydrogen peroxide per kilowatt-hour and a current-yield of 83%. A 5% solution is obtainable when the best current-yield is not insisted on. Experiments with various electrolytes and electrodes gave the same results as at atmospheric pressure.

The investigation of the effect of 1% sulphuric acid under an oxygen pressure of 25 atmos. on the various materials used for electrodes, showed that all metals, with the exception of tin and iron, which go into solution without current being necessary, produce hydrogen peroxide at the same time. Zinc amalgam gives the most hydrogen peroxide, nickel gives a third as much, and then follow the other metals.

T. S. P.

**The Form of Electrolytically Deposited Metals. I. Silver-black.** VOLKMAR KONIGSUTTER and THEODOR TOROPFF (*Zeitsch. Elektrochem.*, 1913, **19**, 161-168. Compare A., 1912 ii, 253, 845).—An account is given of the formation of silver-black by electrolytical methods, of its properties, and the transformation of it into grey, crystalline silver. It is shown that silver-black can be obtained by the action of organic reducing agents on silver solutions, and

also by the action of zinc, copper, and cadmium on dilute solutions of silver salts. Electrolytically, silver-black is best obtained from dilute solutions by the use of comparatively high current density. Silver-black cannot be preserved; no matter how prepared, it speedily changes into grey or white, crystalline silver. The rate of passage into the crystalline variety is about ten times as rapid in the presence of dilute acid as in the presence of dilute alkali, whilst in the latter case the change is quicker than in pure water. Black silver is regarded as in a condition between the colloidal and the crystalline states. This substance when examined microscopically during the electrolytic preparation is seen to be crystalline, but it behaves as a colloid towards electrolytes. At the moment at which the current is stopped, in the preparation of silver-black, it begins to pass over into the grey, crystalline variety, as evidenced by the change in colour and by the shrinking together of the mass. Experiment shows that there is no real volume change in the passage from coherent massive silver to silver-black and to grey, crystalline silver.

To obtain evidence which should indicate the reason for the formation of silver-black, a number of measurements were made on the potential difference of the electrodes during deposition, and from these results it was deduced that the formation in dilute solution is due to the relative lack of crystal centres, so that each discharged ion finds itself more or less isolated, and consequently deposits as such, and does not attach itself to a crystal centre with the formation of the grey, crystalline silver. The sudden change to grey silver on breaking the current is explained as an electro-surface tension phenomenon. The silver-black with very large surface takes up the form of smallest surface on stopping the current, but while the current is flowing and it is negatively polarised the electrostatic repulsions of the charged particles overcome the tendency to a surface diminution. J. F. S.

**The Form of Electrolytically Deposited Metals. II. Silver Deposited by Metals.** VOLKMAR KOULSCHÜTTER, THEODOR TOROPFF, and W. PFANDER (*Zeitsch. Elektrochem.*, 1913, 19, 169—172. Compare preceding abstract).—It is shown that different metals precipitate silver in different, but perfectly definite, conditions, which depend to some extent on the concentration of the silver solution. The experiments were carried out with copper, zinc, cadmium, iron, tin, aluminium, and magnesium. It is shown that the observed differences are due to the velocity with which the precipitation takes place. The addition of neutral salts causes an increase in the velocity of precipitation. This is explained in the following way: In neutral salt solution when copper is the metal, a colloidal copper hydroxide is formed by hydrolysis; this is adsorbed by the copper, and so prevents its further rapid solution, but by the addition of an electrolyte this colloidal substance is removed, either by chemical solution or by coagulation. The addition of such substances as sugar, starch, gum, and gelatin cause the reaction to take place more slowly, but at the same time they cause a very dark powder

to be formed, which is more stable than that usually obtained. The course of the reaction is followed in a few cases by means of potential difference measurements between the depositing metal and the solution.

J. F. S.

### The Form of Electrolytically Deposited Metals. III. The Influence of Foreign Substances on the Deposition of Silver.

VELDMAR KOHLSCHÜTTER and HERMANN SCHACHNER (*Zeitsch. Elektrochem.*, 1913, 19, 172—181. Compare preceding abstracts).—Silver was deposited electrolytically from a 0.05N-solution of silver nitrate, to which had been added just sufficient ammonia to redissolve the precipitated silver oxide; 100 c.c. of this solution were electrolysed after the addition of one or two drops of sodium hydroxide solution, and a small amount of the solution of the metallic nitrate. The nitrates used in the various experiments were those of copper, zinc, cadmium, lead, glaucinum, chromium, aluminium, and thallium. The solutions were electrolysed by a current of 3 milliamperes, which corresponded with a cathode current density of 0.001—0.005 ampere per sq. cm. The silver was deposited in different forms in each case, which were easily reproducible; micro-photographs of the various forms are given in the paper. It is shown that if the solutions are kept more than fifteen to twenty hours quite different forms are obtained, so that in all the experiments described freshly prepared solutions were employed. It is also shown that the amount of silver deposited under these conditions is more than that demanded by Faraday's Law, and that it does not contain more than the merest trace of the added metal. The action of the added substances in producing the different deposits is held to be due to the formation of colloidal metal hydroxides which are deposited on the cathode, and form a type of filter which conditions the distribution of the centres of crystallisation. The excess of silver deposited above that required by Faraday's Law is supposed to be due to causes other than electrolysis, since it does not increase with the concentration of the silver solution.

J. F. S.

### The Form of Electrolytically Deposited Metals. IV. The Deposition of Silver from Solutions of Complex Salts.

VELDMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1913, 19, 181—184. Compare preceding abstracts).—The reasons for the compact adhesive deposition of silver in the electrolysis of complex solutions of silver are discussed in the present paper. It is shown that in the first stages of the deposition colloidal silver in the complex silver compound is deposited; this is demonstrated by the reddish-violet coloration on the cathode, which is the characteristic of the so-called "subhaloids." It is also shown that if a platinum cathode on which this deposit has been formed is removed from the electrolyte and washed, the blue colour vanishes, but that if such an electrode is now placed in a solution of a non-complex silver salt, such as silver nitrate, the further deposition is of the same compact form characteristic of silver deposited from complex solutions, such as  $KAg(CN)_2$ .

It is thought that this first deposit determines the number and position of the crystal centres on which the further deposition takes place. It is shown from theoretical grounds and from analogy to the results of the deposition of foreign metals (see last abstract) that the silver salts are also present in the colloidal form in the complexes, and that these colloids are determinative of the peculiar form of the silver deposition.

Experiments in confirmation of the author's views were made with complex cyanide, thiosulphate, and ammoniacal solutions. The author's views all confirm the work of Danneel (*Zeitsch. Elektrochem.*, 1903, 9, 762), Treiber (A., 1904, ii, 607, 808), and Bodländer and Abegg (A., 1906, ii, 713), which point to the fact that silver deposition is not a secondary reaction due to the primary deposition of potassium, which then reacts chemically to produce silver.

J. F. S.

**Variation of Magnetic Susceptibility with Temperature. II. Aqueous Solutions.** A. E. OXLEY (*Proc. Camb. Phil. Soc.*, 1913, 17, 65—89. Compare A., 1912, ii, 325).—The influence of temperature on the magnetic susceptibility of aqueous solutions of ferric chloride, ferrous sulphate, and ferric nitrate has been examined.

On the assumption that the susceptibility is independent of the intensity of the magnetic field, and that complex molecular aggregates containing water of hydration are formed, the composition of which varies with the temperature in accordance with van Laar's theory, a formula is deduced for the susceptibility  $\chi$ , which may be written in the form  $\chi = A/\theta + B + C\theta$ , where  $\theta$  denotes the absolute temperature. In the case of dilute solutions, this reduces to the simpler form  $\chi = A/\theta + B$ . The experimental observations are shown to be satisfactorily represented by means of these formulae, and this would seem to indicate that if the Curie-Langevin theory is strictly applicable to aggregates, the composition of which is independent of the temperature, the complexity of the aggregates present in the aqueous solutions which have been examined varies with the temperature in accordance with a linear formula.

H. M. D.

**Magnetic Double Refraction and Chemical Constitution.** A. COTTON and HENRI MOTRON (*Ann. Chim. Phys.*, 1913, [viii], 28, 209—243).—A résumé of work published in A., 1906, ii, 146; 1907, ii, 727; 1908, ii, 745; 1909, ii, 773; 1910, ii, 368; 1911, ii, 4; 1912, ii, 426.

H. W.

**The Critical Points of Iron.** WITOLD BRONIEWSKI (*Compt. rend.*, 1913, 156, 699—702).—Using electrolytic iron, the author has studied the variation of its thermoelectric force with respect to copper and platinum, its electrical resistance, and its dilatation with variation in temperature, and curves are given showing these variations. He finds three critical points on the curves, the first

spending with  $\alpha$ -iron, stable below  $730^{\circ}$ , another with  $\beta$ -iron, stable at  $950^{\circ}$ , and the third with  $\gamma$ -iron, stable above  $1020^{\circ}$ . W. G.

**The Thermoelectric Properties of Some Irreversible Nickel and Manganese Steels.** SIEGFRIED HILPERT and FRITZ HERMANN (*Zeitsch. Elektrochem.*, 1913, 19, 215—219).—Steels containing 12.6% and 27.5% of nickel, and 4.58%, 11.7%, and 20.8% of manganese were examined as to their thermoelectric properties after they had been subjected to definite temperatures. The steels after treatment were made into thermo-couples with either constantan or copper, and the two ends subjected to different, but not widely separated, temperatures, and the *E.M.F.*, produced by the temperature difference, measured. With the steel containing 27.5% nickel it is shown that after subjecting the steel to  $-75^{\circ}$  a difference of  $1^{\circ}$  between the ends of the couple produces an *E.M.F.* of 21.1 microvolts, whereas after cooling to  $-185^{\circ}$   $1^{\circ}$  difference gives 7.7 microvolts. From this temperature up to  $400^{\circ}$  the same thermo-electromotive force is produced for  $1^{\circ}$  difference between the ends; after treatment at  $500^{\circ}$  the value rises to 16 microvolts, and at  $600^{\circ}$  it reaches 35.1 microvolts. This case is analogous to the behaviour of the magnetic properties of this steel when it has been subjected to various temperatures (*A.*, 1911, ii, 1057; 1912, ii, 229). Steel with 12.6% nickel showed similar properties to a very slight extent. Steels containing 4.58% and 11.7% manganese, which are strongly magnetic, do not show these properties. It is suggested that the observed differences in the *E.M.F.* have their cause in a considerable volume change, which is accompanied by an internal tension, and that there is a marked hysteresis of the specific volume.

J. F. S.

**The Gas Thermometer as the Basis for High-temperature Measurements.** FRITZ HENNING (*Zeitsch. Elektrochem.*, 1913, 19, 185—192).—A theoretical paper in which the following points, relating to the gas thermometer for use at high temperatures, that is, up to  $1500^{\circ}$ , are discussed: (1) Material of which the thermometer is to be made. (2) Gas with which it is to be filled. (3) Precautions to be taken in use. (4) The dead space. (5) Fixed points to be used in the calibration of such a thermometer. (6) Subsidiary thermometers for controlling temperatures, and for determining the temperatures required for the calculation of the necessary corrections. It is shown that a platinum-iridium vessel is the best for this purpose, and that the dead space can conveniently be brought down to about 1 cubic centimetre. A platinum-platinum-rhodium (10% rhodium) thermocouple is recommended as subsidiary thermometer for temperatures up to  $1100^{\circ}$ , for which the formula for calculation of the temperature is:

$$e = -310 \div 8.045t - 0.00172t^2 \text{ microvolt.}$$

Above  $1100^{\circ}$  to  $1600^{\circ}$  it can still be used, but the temperature is obtained from the formula:  $e = 30600 \log(1.3 \div t^2 \times 10^{-6}) - 1590$ . As fixed points for controlling the temperatures, the following melting and boiling points are recommended: Naphthalene, b. p.  $218.0^{\circ}$ ;



tin, m. p.  $231.8^{\circ}$ ; benzophenone, b. p.  $305.9^{\circ}$ ; cadmium, m. p.  $320.9^{\circ}$ ; zinc, m. p.  $419.4^{\circ}$ ; sulphur, b. p.  $444.5^{\circ}$ ; antimony, m. p.  $630^{\circ}$ ; aluminium, m. p.  $658^{\circ}$ ; silver, m. p.  $961^{\circ}$ ; gold, m. p.  $1063^{\circ}$ ; copper, m. p.  $1084^{\circ}$ ; nickel, m. p.  $1452^{\circ}$ ; cobalt, m. p.  $1490^{\circ}$ ; and palladium, m. p.  $1587^{\circ} \pm 12^{\circ}$ . J. F. S.

**A Simple Method for Maintaining Constant Temperatures in the Region of the Room Temperature.** FRITZ BAHR (*Zeitsch. angew. Chem.*, 1913, 26, 135).—The action of the gas regulator in a thermostat working at the ordinary temperature may be assisted by regulating the flow of water by means of a sensitive syphon. For this purpose a hole is blown in a piece of glass tubing, which is then drawn out at this point, and cut off across the narrow slit. The tube is then bent near the end through  $360^{\circ}$ , so as to form a syphon, which is then hung in the full thermostat. J. C. W.

**The Specific Heat of Bismuth Oxide.** OTTO HAUSER and W. SIEGER (*Zeitsch. anorg. Chem.*, 1913, 80, 1—6).—The specific heat of bismuth oxide,  $\text{Bi}_2\text{O}_3$ , has been determined by heating the oxide, enclosed in a silver case, to a temperature of  $100$ — $507^{\circ}$  in an electric furnace, and then rapidly dropping into a copper calorimeter enclosed in a vacuum vessel. The values obtained are:  $20$ — $100^{\circ}$ ,  $0.0568$ ;  $20$ — $312^{\circ}$ ,  $0.0604$ ;  $20$ — $503^{\circ}$ ,  $0.0623$ .

It has not been found possible to dehydrate bismuth peroxide without loss of oxygen. C. H. D.

**Effect of High Pressures on the Physical and Chemical Behaviour of Solids.** JOHN JOHNSTON and LEASON H. ADAMS (*Amer. J. Sci.*, 1913, [iv], 35, 295—253\*).—In any discussion of the influence of pressure on solid systems, it is necessary to distinguish between the effects of uniform pressure and of non-uniform pressure. The effects produced by non-uniform compression are in general such that the original state of the system is not re-established when the pressure is released. Most of the work on the influence of high pressures on solids has been carried out under these conditions, and it seems probable that many of the apparently contradictory statements recorded in the literature are due to the disregard of the distinction between the two types of compression.

In general, uniform pressure raises the melting point by an amount which seldom exceeds  $10^{\circ}$  per 1000 atmospheres; its effect on solubility is also very slight. Non-uniform pressure, on the other hand, always lowers the melting point and raises the solubility, and by amounts which are many times greater than the corresponding variations produced by the application of uniform pressure. The actual cause of the phenomena recorded as occurring when solid systems are subjected to high pressure is supposed to be the local melting produced by non-uniform compression, and on the assumption that permanent deformation of a crystalline aggregate is always conditioned by liquefaction, it is found that the pressure required to produce this change at the ordinary temperature is well within the bounds of probability.

\* and *Zeitsch. anorg. Chem.*, 1913, 80, 281—331.

From an examination of the available data, and in particular of the results obtained by Spring, the authors draw several conclusions with respect to the physical and chemical behaviour of solids under high pressures.

The pressure necessary to produce local melting of crystalline aggregates depends mainly on the melting point, the heat of fusion, the density of the substance, and the temperature at which the compression is applied. Generally speaking, those substances which, at a given temperature, require the largest pressures to weld them, are those which have the highest melting points.

Compression alone will not in general produce crystallisation or bring about the transformation of one modification of a substance into another. If the conditions are such that the velocity of transformation is appreciable, it may give rise to such changes in certain cases; and if, further, the conditions are such that partial melting may occur, then the compression will be followed by a partial transformation.

In regard to chemical reactions between solids, non-uniform pressure will also have a much greater effect than uniform pressure. In the latter case, the reaction can only occur at the surfaces of contact between the solids, whereas the conditions obtaining with non-uniform compression will assist the reaction by a renewal of the contact surfaces in consequence of local melting and the flowing away of the fusion. With reference to the alleged reaction between barium sulphate and sodium carbonate and between potassium nitrate and sodium acetate, it is pointed out that the methods adopted in the examination of the product after compression afford no certain information as to the actual condition of the dry mixture.

Apart from the question of the direct influence of pressure on reactions between solids, it is probable that the more intimate contact which is attained under pressure will result in an increased rate of interdiffusion of the substances, and to this extent pressure will have an influence on the reaction. The formation of alloys may be referred to as a special case of such interaction. Where the formation of solid solutions is possible, pressure will have an effect by promoting indirectly the rate of diffusion, but there is no evidence in the available data to show that compression itself has any specific influence on the formation of alloys. H. M. D.

**Fusibility of Natural Fats.** HENRI LE CHATELIER and (Mlle.) CAVALLONAC (*Compt. rend.*, 1913, 156, 589-594). The authors have made a careful study of the temperatures of fusion and solidification of two natural fats, vegetalin and stearin, under varying conditions, and find that they obey the general laws of change of state in that their fusion and solidification is a reversible phenomenon the temperature of which can be determined to one-tenth of a degree by sufficient experiments. The melting point as rapidly determined does not, as a rule, differ by more than a degree from the true value; the solidification temperature, however, shows greater variation. Foreign substances have a marked effect on the

melting point, and these fats exhibit the phenomenon of <sup>sub.</sup> fusion. W. G.

**Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. II. Mixtures containing Unsymmetrical Constituents.** PAUL PASCAL and LÉON NORMAND (*Bull. Soc. chim.*, 1913, [iv], 13, 207-216).—The authors have examined the melting-point curves of a series of mixtures composed of the following pairs of constituents: (1) dibenzyl and benzyl aniline, (2) azobenzene and benzylideneaniline, (3) stilbene and benzylideneaniline, (4) benzylideneaniline and benzylaniline, (5) phenyl benzyl ether and benzylaniline, (6) phenyl benzyl ether and dibenzyl, (7) benzylaniline and hydrazobenzene, (8) dibenzyl and benzylideneaniline, (9) hydrazobenzene and benzylideneaniline, (10) toluene and benzylideneaniline, (11) benzylaniline and azobenzene, (12) benzylaniline and stilbene, and (13) toluene and benzylaniline. In every case a eutectic mixture was obtained. In the first seven cases, in which the constituents of the mixtures have either different central atoms or different central linkings, the extent of the region of syncrystallisation (defined by the difference in percentage of either of the constituents of the mixed crystals which form the eutectic mixture) lies between 20% and 40%, whilst in the last six cases, in which the constituents of the mixtures possess different central linkings and central atoms, it lies between 40% and 60%, attaining a maximum of 65% in the case of mixtures of toluene and benzylaniline. H. W.

**The Fusion Curves of Several Substances.** ERNST AUGER-BLOCK (*Zeitsch. physikal. Chem.*, 1913, 82, 403-438).—A method due to Tammann is used for the determination of the equilibrium pressure in the melting of the substances: veratrole, *p*-chlorotoluene, *p*-iodotoluene, *p*-bromotoluene, anethole, diphenylmethane, dichlorobenzene, benzylaniline, thymol, and menthol. It is shown that the equilibrium pressure is independent of the proportions of crystalline and liquid substance, and a method is given for ascertaining whether the substance under examination is pure. If the substance is pure, the equilibrium pressure is constant for all proportions of melted and crystalline substance, but if impure the equilibrium pressure increases very rapidly when only a small proportion of the substance is melted. The fusion curves of the ten substances mentioned above are determined for pressures 1-3000 kilog. by Tammann's method, and the temperature readings compared with those calculated by the Tammann formula:

$$t = t_p + ap - bp^2.$$

The agreement is very good, the differences being in every case smaller than the mean probable error. The substances examined are, according to the Eötvös formula, non-associated when molten, and, according to the Tammann theory (this vol., ii, 193), should only form one kind of crystals. This statement is confirmed by the melting curves obtained. It is, however, remarkable that two of these substances, menthol and veratrole, are known to exist in a

second unstable form. The fusion curve for benzene is determined by means of a series of determinations of  $pT$  curves at constant volume. The method is due to Tammann (A., 1912, ii, 630). The curve is determined for pressures up to 3050 kilog., and the temperature values are found to agree with those calculated by the Tammann formula:  $t = 5.46 + 0.0283p - 0.00000196p^2$ , within limits of  $-0.25^\circ$  and  $-0.26^\circ$ , the mean divergence being  $0.03^\circ$ . It is shown that the coefficient  $dp/dt$  is smaller for the molten substance than for the crystalline substance, and that the value increases for both with increasing pressure. These two facts are both in accord with the Tammann theory (*loc. cit.*). The value  $dp_p$  is not constant for the different  $pT$  curves, but increases with increasing temperature. It is shown that the quantity of material employed is without influence on the  $p$  and  $T$  values of the equilibrium point between liquid and crystals, but that the  $dp_p$  values are smaller at low temperatures for smaller amounts of material than for larger amounts. This is explained by a change in the apparent compressibility of the material. The volume change  $\Delta v_p$  at constant temperature and constant pressure, in melting is redetermined for benzene. The values obtained confirm the Tammann formula (*loc. cit.*), and are also in good agreement with those of Tammann and Cowper (A., 1910, ii, 20). The fusion curve of Glauber's salt is determined by means of  $pT$  curves, and agrees well with that calculated from Tammann's formula:  $t = 32.6 + 0.000591p - 0.00000055p^2$ . A method is described by which impurities may be removed from the substances examined. Finally, the relationship between the fusion curves of different substances is discussed. It is shown that the ratio between the absolute melting points of two substances at the same pressure is a constant. This formula is of the same nature as that given by Ramsay and Young for the vapour pressures. The relationship is examined for twenty pairs of substances up to pressures of about 3000 kilog., and for a given pair shown to hold very well. The constant varies for different pairs between 0.9733 for aniline and water, and 1.2210 for diphenylamine and aniline. It is further shown that  $T_2/T_1 = T'_2/T'_1 = c$ , where  $T_1$  and  $T_2$  are the melting points at a given pressure for a pair of substances, and  $T'_1$  and  $T'_2$  are the melting points of the same substances at a second pressure, and  $c$  is a constant. The value of  $c$  varies from zero for the pair benzylaniline, aniline to  $-0.0060$  for aniline, water, whilst sodium potassium gives  $-0.00139$ , the divergence being in all cases well within the experimental error. J. F. S.

**Molecular Attraction.** K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1913, 82, 541—574).—A mathematical paper, in which an attempt is made to deduce a formula which shall give the molecular attraction. The general form of the Newton Law of Gravitation,  $F = m^2k/r^2$ , is made the basis of the calculations. It is found that if  $n = 5, 6$ , or 7, the formula represents in some cases the observed conditions, obtained from the heat of vaporisation. In general, the value  $n = 6$  is better than the other values. A formula is also deduced for calculation of the heat of vaporisation, which has the

form  $(C - 2.52 - C_2)/L\beta - K = 1.63$ , in which  $\beta$  is the coefficient of cubical expansion,  $L$  the heat of vaporisation,  $U$  the molecular heat, 2.52 cal., the quantity of heat used up in increasing the velocity of the molecules, and  $C_2$  the quantity of heat used in intra-molecular work. The formulæ which are deduced from considerations of the potential of the molecules are used for calculating the heat of vaporisation of several substances, and shown to hold within 2—3%.

J. F. S.

**The Latent Heat of Vaporisation of Metals.** EDMOND VAN AUBEL (*Compt. rend.*, 1913, 156, 456—457).—The author has calculated the constant in Trouton's Law for the metals mercury, cadmium, zinc, and bismuth, using the values obtained by Wehnelt and Musceleanu (this vol., ii, 23) for their latent heats of vaporisation, and finds that they obey the above law. Taking the value for this constant as 20, he calculates the boiling point of magnesium as 1792°.

W. G.

**Mechanism of Evaporation.** RENÉ MARCELIN (*J. Chim. phys.*, 1912, 10, 680—690).—The rate at which the meniscus is lowered by evaporation in capillary tubes containing "superheated" ether or carbon disulphide at a constant pressure is measurable by cathetometer and stop-watch. The surface layer is cooled by evaporation to the temperature at which it is in equilibrium with the vapour at the given pressure. The rate at which evaporation takes place is therefore governed by the rate at which heat is conducted through the glass tube from the thermostat under the temperature gradient which establishes itself near the meniscus; thus the rate of evaporation,  $r_p = M(T_b - T_p)/rdL$ , where  $M$  is a constant depending on the thickness and heat conductivity of the glass,  $T_b$  is the temperature of the thermostat,  $T_p$  is the temperature of the surface layer corresponding with vapour pressure  $p$  for the given liquid,  $r$  is the radius of the tube,  $d$  the density of the liquid, and  $L$  its latent heat.

This formula was verified experimentally, and the same constant  $M$  was obtained with ether as with carbon disulphide at a variety of temperatures and pressures, and also with tubes of different bore, but the same thickness of wall. The real rate of evaporation is apparently at least ten times as great as the apparent rate in these experiments.

It is deduced from the kinetic hypothesis that in a liquid of molecular weight  $M$  and vapour pressure  $P$  at temperature  $T$  evaporating into a vapour phase at pressure  $p$ , the rate of evaporation  $r = \alpha(P - p)/4d \times \sqrt{(3M^*/RT)}$ , where  $\alpha$  is a fraction representing the proportion of the gaseous molecules which are re-absorbed on collision with the liquid surface.

The highest values of  $r$  observed lead to  $\alpha = 1/100$  as a minimum, but in view of the lowering of the surface temperature in the experiments  $\alpha$  is probably greater than 1/10.

The author's method lends itself to the evaluation of the boiling points or vapour pressures of pure liquids. The variation of

with  $T$  at any constant pressure  $p$  being a linear function, the curve can be extrapolated to  $e=0$ , when  $T$  becomes the boiling point at pressure  $p$ .

R. J. C.

**Chemical Affinity. VIII. Crystalline Change of the Alkali Salts.** JOHANNES N. BRÖSTED (*Zeitsch. physikal. Chem.*, 1913, **82**, 621–640. Compare A., 1911, ii, 381, 856; 1912, ii, 736).—A continuation of the work contained in the previous papers. The double decomposition of various pairs of alkali salts is investigated in the present paper. The solution affinity and the affinity of the double decomposition are determined. To arrive at these quantities the values of the dilution affinity, solubility, and vapour pressure of the solutions at the temperature of the experiments must be known. These values have been determined in the present work. The dilution affinity is calculated from freezing-point measurements for sodium chloride, sodium nitrate, sodium chlorate, sodium bromide, sodium sulphate, sodium fluoride, potassium iodide, potassium fluoride, potassium chlorate, potassium sulphate, potassium nitrate, and potassium chloride. From these measurements it is seen that work of dilution is generally less for a potassium salt than for the corresponding sodium salt. The solubilities of the above-mentioned salts at  $100^\circ$  are determined, and the following values obtained in grams per 100 grams water: KBr=195.3; NaCl=39.22; NaI=303.4; NaBr=121.9; NaClO<sub>3</sub>=204.9; NaNO<sub>3</sub>=176.3; KCl=56.05; KI=207.7; KClO<sub>3</sub>=57.7; KNO<sub>3</sub>=214.8; Na<sub>2</sub>SO<sub>4</sub>=42.19; K<sub>2</sub>SO<sub>4</sub>=24.1. The vapour pressures of the saturated solutions of the above salts at  $100^\circ$  were also determined, and the following values obtained: NaCl=561.5 mm.; NaBr=332.9; NaI=174.4; NaF=734.0; NaClO<sub>3</sub>=410.0; NaNO<sub>3</sub>=418.9; Na<sub>2</sub>SO<sub>4</sub>=684.7; KCl=567.8; KBr=526.3; KI=127.0; KF=174.3; KClO<sub>3</sub>=668.3; KNO<sub>3</sub>=496.0; K<sub>2</sub>SO<sub>4</sub>=723.9. From these data the energy change in the double decomposition of pairs of the salts mentioned is calculated, and the following results obtained: NaF+KCl→NaCl+KF–6830 cal.; NaF+KBr→NaBr+KF–8520 cal.; NaF+KI→KF+NaI–10150 cal.; NaCl+KBr→KCl+NaBr–1690 cal.; NaCl+KI→KCl+NaI–3320 cal.; NaBr+KI→NaI+KBr–1630 cal.; NaCl+KNO<sub>3</sub>→NaNO<sub>3</sub>+KCl–840 cal.; NaCl+KClO<sub>3</sub>→NaClO<sub>3</sub>+KCl–2270 cal.; NaCl+ $\frac{1}{2}$ K<sub>2</sub>SO<sub>4</sub>→ $\frac{1}{2}$ Na<sub>2</sub>SO<sub>4</sub>+KCl–340 cal.; NaNO<sub>3</sub>+KClO<sub>3</sub>→NaClO<sub>3</sub>+KNO<sub>3</sub>–1430 cal. The values obtained above by the new method are compared with those obtained by the older electrochemical method (*loc. cit.*), and a very good agreement is found between them. In the double decomposition between haloids of sodium and potassium, the tendency is, that the two elements of lowest atomic weights and those of highest atomic weights will combine.

A. P. S.

**Fractional Distillation with Steam.** L. GURWITZCH (*Zeitsch. angew. Chem.*, 1913, **26**, 102–103).—From a consideration of the formula put forward by Vresvski (A., 1910, ii, 1033) for the composition of the vapour given off from a mixture of volatile liquids, the author deduces that when the temperature of

vaporisation of such a mixture is lowered, the proportion of the constituent with the lesser molecular latent heat of vaporisation should increase in the vapour phase. The temperature of vaporisation is lowered by steam distillation, and, therefore, in the case of a mixture of homologues, the proportion of the more volatile constituents should increase in the distillate.

The above deduction has been verified by experiments with a purified Russian illuminating oil (Meteor oil), consisting of a mixture of saturated hydrocarbons and naphthenes. In order to avoid dephlegmation, the whole of the distilling flask, together with the greater part of the side-tube, was immersed in the oil-bath. Instead of passing steam through the flask, water was added to the contents, together with numerous pieces of pumice stone, so that the surface of contact between the water and the oil should be as great as possible.

T. S. P.

**Triferrocabide (Cementite),  $\text{Fe}_3\text{C}$ .** OTTO RUFF and EDWARD GERSTEN (*Ber.*, 1913, **46**, 391—400).—Jermilov (*J. Russ. Metall. Soc.*, 1911, 357—366) has found that the molecular heat of formation of triferrocabide is  $+2.27$  Cal., whereas the authors have previously found it to be  $-15.1$  Cal. (*A.*, 1912, ii, 260). In the authors' calculations the only thermochemical datum which had not been determined by themselves was the heat of oxidation of ferrous oxide to ferroso-ferric oxide ( $\text{Fe}_3\text{O}_4$ ), the value used being that due to Le Chatelier. They have consequently redetermined this value, and find  $28.6 \pm 1.8$  Cal. as the heat of oxidation of  $\text{FeO}$  to  $\frac{3}{4}\text{Fe}_3\text{O}_4$ , which is in fairly good agreement with Le Chatelier's value,  $25.7$  Cal. Using this value, the molecular heats of formation given in the previous paper (*loc. cit.*) are corrected to the following values:  $\text{Fe}_3\text{O}_4$ ,  $267.1 \pm 0.2$  Cal.;  $\text{FeO}$ ,  $60.4 \pm 1.8$  Cal.;  $\text{Fe}_3\text{C}$  (from  $\alpha$ -iron and graphite),  $-15.3 \pm 0.2$  Cal. The value for triferrocabide is thus practically unaltered. Jermilov's value is due to the fact that he has taken too high values for the molecular heats of formation of  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$ .

T. S. P.

**Heat of Formation of Additive Organic Compounds. I. Picrates.** BAROLO L. VANZETTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 103—109).—The following heats of formation have been determined: naphthalene picrate (in two experiments), 1450 cal., 951 cal. (compare Brönsted, *A.*, 1912, ii, 21); isosafrole picrate, 4430 cal. (mean of five experiments); eugenol picrate, 5910 cal.; 2-methylindole picrate, 2082 cal.

R. V. S.

**Physico-chemical Investigations with Aromatic Stereoisomeric Acids. I.** WALTER A. ROTH and RICHARD STOURMER (*Ber.*, 1913, **46**, 260—280).—The mol. heats of combustion, dissociation constants, and solubilities of a number of carefully purified isomeric acids have been determined. The general rule indicated by Stohmann (*A.*, 1892, ii, 153) that the stable acids have the lower heats of combustion and smaller dissociation constants, is confirmed. Some liquid esters have also been calorifically and optically

examined. The results are given in the following table, where  $1/\text{min.}$  is the reciprocal of the solubility, that is, the number of litres of water required to dissolve 1 Mol. at 25°.

Substance.	M. p.	Heat of combustion.	Dissociation constant $\times 10^{-4}$ .	$1/\text{min.}$
Cinnamic acid.....	132-137	1911.4 Cal.	3.34	270
<i>o</i> -Cinnamic acid .....	53	1918.1	14.49	17.5
Methylcinnamic acid .....	182-183	1932.4	2.97	2129
Ethylcinnamic acid .....	91-92	1938.6	5.40	259
Ethylcinnamic acid .....	133-134	1917.9	2.12	2110
Ethylcinnamic acid .....	101-102	1921.1	4.51	333
Propylcinnamic acid .....	105-106	1472.0	—	—
Propylcinnamic acid .....	83-84	1477.9	—	—
Butylcinnamic acid .....	89-90	1632.4	—	—
Butylcinnamic acid .....	55-54	1638.8	—	—
<i>p</i> -Amylcinnamic acid.....	79-71.5	1791.5	1.4	11909
<i>p</i> -Amylcinnamic acid .....	80-80.5	1793.1	1.21	2670
<i>p</i> -Amylcinnamic acid .....	154-155	1299.9	5.0	1130
Angeliccinnamic acid .....	85	1215.1	11 (approx.)	189
Phenylacrylic acid.....	238	1668.8	2.5	7999 (approx.)
<i>o</i> -Methoxyacrylic acid .....	99-100	1677.8	10.91	466
<i>p</i> -Hydroxycinnamic acid .....	296	992.1	2.34	126
<i>o</i> - <i>p</i> -Hydroxycinnamic acid .....	126-127	997.5	8.14	41.6
<i>p</i> -Methoxycinnamic acid .....	170	1044.2	2.1	2564
<i>o</i> - <i>p</i> -Methoxycinnamic acid .....	66	1173.6	9.29	969

Ethyl methylcinnamate: h. p. 291-292.5°. Heat of combustion, 1495.7 Cal.;  $D_4^{25}$  1.4016;  $n_D$  1.54697;  $n_F$  1.55399;  $n_H$  1.57303.

Methyl ethylcinnamate: h. p. 306-307°. Heat of combustion, 1491.8 Cal.;  $D_4^{25}$  1.0998;  $n_D$  1.56318;  $n_H$  1.57188;  $n_F$  1.59680;  $n_H$  1.6033.

Methyl ethylcinnamate: h. p. 288.5-289.5°. Heat of combustion, 1496.5 Cal.;  $D_4^{25}$  1.0981;  $n_D$  1.54724;  $n_H$  1.55431;  $n_F$  1.57381.

The compounds marked with an asterisk are new, and will be described in a future paper, whilst the majority of the others are the fruit of Stoermer's researches (A., 1910, i, 111; 1911, i, 295).

The "heat values" for particular substituents agree with Stohmann's; for example, the heats of combustion of the methyl esters are about 173 Cal. higher than those of the free acids. The proximity of the substituent to the carboxyl group has a great influence on the dissociation constant. Whereas *o*-methoxybenzoic acid has the constant  $8.15 \times 10^{-5}$ , methyl cinnamic acid has the value  $2.97 \times 10^{-5}$ , and methyl coumarinic acid,  $5.4 \times 10^{-5}$ . A relation is established between the amount of transformation which takes place when the stable acid is exposed to ultraviolet light, and the ratio of the dissociation constants. When this ratio is smallest the transformation is most complete.

The optical properties of the three esters agree with those of the esters of non-substituted cinnamic acids described by Brühl (A., 1897, ii, 129). The stable forms have the higher densities and refractive indices, whilst an ether group in the ortho-position raises the specific rotation slightly and the dispersion considerably.

J. C. W.



**Densities at the Critical Point.** MAURICE PRUD'HOMME (*J. Chim. phys.*, 1912, 10, 636—639).—According to van der Waals' equation, the critical volume should be three times the volume at absolute zero, but as is well known, for many substances it assumes a value in the neighbourhood of four times. When van der Waals' equation is solved for density it is found that the three roots:

$$d_1 + d_2 + d_3 = m/b = \text{a constant} = m/n_1b + m/n_2b + m/n_3b,$$

where  $m$  is the molecular weight. At the critical point where the densities of vapour and liquid become equal,  $d_1 = d_2$ . Hence  $2/n_1 + 1/n_3 = 1$ . This equation has only two solutions in integers, namely,  $n_1 = n_3 = 3$  and  $n_1 = 4, n_3 = 2$ .

The first solution is the ordinary one, where  $V = 3b$ . The second solution corresponds with the exceptional cases (formates, methyl acetate, fluorobenzene, etc.), where  $V = 4b$ , but it remains to give an explanation of the third root, namely,  $V = 2b$ , the density  $d_3$  being twice the critical density, that is,  $d_3 = d_1 + d_2$ . According to Cailletet and Mathias ( $d_1 + d_2$ ) is a linear function of the temperature, whether  $n$  is normal or not. Hence,  $d_3$  is also a linear function of the temperature, and in the exceptional cases an infinitesimal variation in the temperature corresponds with a variation in  $d_3$  which is the sum of the variations in  $d_1$  and  $d_2$ .

The author interprets  $d_3$  as representing the density of the surface film separating the liquid from the vapour. At the critical point the density in the surface film must be twice the critical density for the substances mentioned.

R. J. C.

**Pressure, Density, and Expansion of Saturated Water Vapour.** KONRAD W. JURISCH (*Zeitsch. physikal. Chem.*, 1913, 82, 385—402).—A theoretical mathematical paper, in which the relationships of the pressure, density, and expansion are discussed.

J. F. S.

**The Influence of Dissociation on the Density of Saturated Water Vapour.** KONRAD W. JURISCH (*Zeitsch. physikal. Chem.*, 1913, 82, 575—580; see also preceding abstract).—A mathematical paper, in which it is shown that the maximum density of water vapour lies at  $T = 98.5^\circ$ . The diminution of density at higher temperatures is shown to be due entirely to a dissociation of the water vapour; a minimum density lies approximately at  $T = 226^\circ$ , at which point 55.66% is dissociated.

J. F. S.

**The Influence of Dissociation on the Expansion of Saturated Water Vapour.** KONRAD W. JURISCH (*Zeitsch. physikal. Chem.*, 1913, 82, 581—586; see also preceding abstracts).—A mathematical paper, in which it is shown that there is a maximum of the expansion at  $T = 1000^\circ$  and a minimum at  $T = 1170^\circ$ . It is shown that this is due entirely to the dissociation, since this is the only volume changing function which is operative in the region mentioned (see last abstract).

J. F. S.

The Temperature-coefficient of the Molecular Surface Energy and the Molecular Cohesion. PAUL WALDEN and RICHARD SWINNE (*Zeitsch. physikal. Chem.*, 1913, 82, 271—313. Compare A., 1911, ii, 97; 1912, ii, 628).—New determinations of the density and surface tension of a number of substances are given for temperatures between 20° and 100°. The substances investigated are: octinene, undecinene, hexa-ethylbenzene, myricyl alcohol, the triethyl ester of aconitic acid, diethyl ester of sebacic acid, diisooamyl ester of sebacic acid, *l*-amyl ester of bromo-*n*-butyric acid, tetrachloroethane, tetrabromoethane, and dichlorobromomethane. The specific cohesion, free surface tension, free molecular surface energy, and the temperature-coefficients of the free molecular surface energy ( $dMa^2/dt$ ) and molecular cohesion,  $dE_0/dt$ , were calculated. The results obtained in these experiments are compared with similar values calculated by other investigators, and it is shown: (1) That the coefficients  $dMa^2/dt$  and  $dE_0/dt$  increase as an homologous series is ascended. (2) That the substitution of hydrogen by the ethyl group causes an increase in the coefficients for members of the benzene series. (3) For alcohols the coefficient  $dMa^2/dt$  increases very much as the series is ascended. (4) The replacement of hydrogen by chlorine, iodine, or bromine causes an increase in the coefficients, which is greatest in the case of the iodine substitution and least in that of chlorine.

It is also shown that replacement of oxygen by sulphur causes the value  $dMa^2/dt$  to increase. The replacement of an atom of lower atomic weight by one of higher atomic weight causes the coefficient  $dMa^2/dt$  to increase. This is demonstrated in the case  $\text{CCl}_4 \rightarrow \text{SiCl}_4 \rightarrow \text{SnCl}_4$ . For eight of the substances investigated the value  $dE_0/dt$  exceeds the normal value given by Ramsay and Shields, and in consequence these substances ought to be regarded as dissociated. On the other hand, the Dutoit-Mojou vapour pressure expression (A., 1909, ii, 470) and the Walden expression for the value  $dE_0/dt$  (A., 1908, ii, 1014) point to these liquids being normal. The Ramsay-Shields formula for the normal value of  $dE_0/dt$  is discussed, as also is the Gnye theory of the dissociation in the surface layer. It is shown that the values  $dMa^2/dt$  and  $dE_0/dt$  are of an additive nature, and from an examination of 316 substances formulae are deduced which give a means of calculating these coefficients. The formulae for normal liquids are:

$$dMa^2/dt = -[0.00027(\Sigma \sqrt{A}) + 0.0103],$$

$$dE_0/dt = -[0.011(\Sigma \sqrt{A}) + 1.90],$$

where  $\Sigma \sqrt{A}$  is the sum of the square roots of the atomic weights of the component atoms.

The agreement between the values of the coefficients calculated by the above formulae and those obtained from experimental results is, on the whole, good. For elements and halogen derivatives the agreement is best; for hydrocarbons a variation of about 12% is found in some cases; esters, 6% is about the maximum divergence; oxides, 9% divergence, but the agreement is generally good; amines,

a mean divergence of about 10%, but some amines differ far more than this figure. Nitro-compounds, acid amides, nitriles, and hydroxy-derivatives are less in accord with the formulæ. J. F. S.

**Dimensions of the Surface Energy of Solid Substances.** WILLIAM J. JONES (*Zeitsch. physikal. Chem.*, 1913, 82, 448—456).—The formulæ used by Ostwald (A., 1900, ii, 730), Hulett (A., 1901, ii, 493), and Freundlich for calculating the surface energy of solid substances are critically discussed. The author deduces a formula from considerations of a thermodynamical reversible process, which he applies to the experimental data of Hulett (*loc. cit.*). The formula is given by:

$$2\sigma[\rho(1/r_2 - 1/r_1) - RT/M\{(n-1)(\gamma_1 - \gamma_2) - n/m - 1 \log_e(1 - \gamma_1)/(1 - \gamma_2) + m/(m-1) \cdot \log_e \gamma_1/\gamma_2\}]$$

in which  $r_1$  and  $r_2$  are the radii of the solid particles which are dissolving and being formed in the saturated solution,  $\sigma$  the surface energy per unit area,  $\rho$  the density of the solid,  $\gamma_1$  and  $\gamma_2$  the degrees of dissociation of the solid substance of radii  $r_1$  and  $r_2$  in the saturated solutions,  $m$  is a constant having a value between 1.35 and 1.55,  $M$  is the molecular weight,  $n$  is the number of ions furnished by the salt, and  $R$  and  $T$  have their usual meanings. The surface energy for gypsum calculates to 1050 ergs. per sq. cm., and for barium sulphate the value 1300 ergs. per sq. cm. is obtained.

J. F. S.

**Method of Determining "a" of van der Waals' Equation from the Surface Tension.** ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, 17, 154—161).—The various known methods of computing  $a$  involve the assumption that  $b$ , the real molecular volume, is unaffected by changes of temperature and pressure. The author's method, which is based on the surface tension formulæ of Young and Eötvös, is independent of any assumption as to the value of  $b$ .

Young's formula,  $S = rK/3$ , equates the surface tension to the radius of action  $r$  of cohesive attraction and the total cohesive pressure  $K$ . The rival formula,  $S = 3rK/20$ , due to Rayleigh, is rejected by the author because it leads to improbable values of  $a$  according to his method of treatment.

van der Waals' constant  $a$ , which expresses the cohesive power may be equated to  $NM^2K$ , where  $N$  is the number of molecules in volume  $V$ . Hence,  $a/V^2 = M^2K/v^2$ , where  $v$  is the space occupied by a single molecule. At absolute zero, when the molecules are in contact,  $v = v_0$ . Hence,  $Sv_0^2 = M^2K/3v_0$ .

Now, according to Eötvös' formula,  $Sv_0^2 = 2.19(T_c - 6)V/V_c$ . By equating the two values of  $Sv_0^2$  and assuming  $N$  to have the value  $6.21 \times 10^{23}$ , the author deduces that  $M^2K = 9.045 \times 10^{-26}(T_c - 6)/V_c$ . From  $M^2K$ ,  $a$  and  $b$  can readily be calculated.

The values of  $b$ , thus calculated for ether, pentane, and octane are shown to be a constant fraction of the critical volume:  $V_c/b_c = 2.074$ . This figure is very close to the various estimates by

van der Waals, and departs considerably from the theoretical value, namely, 3.

The values of  $M^2A$  calculated by the author for twenty-seven substances with the aid of Young's surface-tension data are very similar to the values obtained by the ordinary formula, but in some instances differ markedly from these. The new formula is considered to give the more accurate values because these exhibit more clearly the relationship of cohesion to molecular weight and valency deduced by the author.

R. J. C.

**Properties of a Liquid Connected with its Surface Tension.** RICHARD D. KLEMAN (*Proc. Camb. Phil. Soc.*, 1913, 17, 149-159. Compare this vol., ii, 26). In the previous paper a formula was deduced for the surface tension of a liquid on the assumption that there is no transition layer at the surface. By substitution of the experimentally determined surface tension, the formula may be inversely applied to calculate the absolute weight of a molecule. From the data for ethyl ether, carbon tetrachloride, methyl formate, and benzene, the mean weight of the hydrogen atom, which is obtained from the formula, is  $1.56 \times 10^{-24}$  gram. This is in good agreement with the value  $1.61 \times 10^{-24}$  gram obtained by Rutherford from experiments on the  $\alpha$ -particle.

A number of relations have also been obtained connecting the surface tension of a liquid with its internal heat of vaporisation, compressibility, coefficient of expansion, and other quantities. Some of these may be utilised for the detection of association and estimation of the extent to which association occurs.

H. M. D.

**Determination of the Viscosity of Caoutchouc Solutions.** J. G. FOL (*Chem. Weekblad*, 1913, 10, 154-174).—From the results of a number of determinations of the viscosity of a specimen of caoutchouc from Java, the author makes the following inferences: (1) In the determination of relative viscosity the type of viscometer employed has an important influence on the results. (2) The diameter of the capillary in Ostwald's viscometer should not be too small. (3) Violent shaking during the making of the solution considerably affects the viscosity. (4) There is a remarkable relation between the relative viscosity of caoutchouc solutions of similar concentration. (5) The viscosity is affected by the length of time which has elapsed between the preparation of the solution and the determination, especially for solutions of high concentration. (6) The relative viscosity of the solutions of the samples examined was affected by the temperature, but not the absolute viscosity. (7) With concentrated solutions the time of efflux diminishes between successive determinations, the greatest difference being observed between the first and second reading.

Details of a method of determining the viscosity of caoutchouc solutions are given.

A. J. W.

**Relationship between Molecular Weight and Turbulence Viscosity Constant.** WALTHER SOERBY (*Physikal. Zeitsch.*, 1913, 14, 147-152. Compare A., 1911, 5, 793; 1912, ii, 900).—From  
\* and *Zeitsch. Chem. Ind. K.*, 1913, 12, 131-137.

experiments on the hydraulic flow of methyl propionate, propyl acetate, and butyl acetate at temperatures between  $15^{\circ}$  and  $40^{\circ}$ , it is found that the connexion between the time of flow ( $t$ ), the pressure ( $p$ ), and the temperature ( $\theta$ ) in the primary stage of turbulence is expressed by  $t = C/p^{0.658} \cdot e^{\theta/273}$ . The value of  $C$  for ethyl acetate is 114.3, methyl propionate 115.2, propyl acetate 135.8, and for butyl acetate 130.2. The constant  $C$  appears to be related to the molecular weight ( $M$ ) by means of the equation  $C = 12.25 \sqrt{M}$ .

In the third stage of turbulence, in which under very high pressures the liquid appears to be projected through the capillary like a frictionless, solid, cylindrical column, the time of flow is given by  $t = C'/\sqrt{p}$ , in which  $C'$  is equal to 33.4 for butyl acetate, 34.0 for propyl acetate, 34.6 for ethyl acetate, and 34.8 for methyl propionate.

The sequence, which is obtained when the esters are arranged according to the viscosity constants, is thus seen to be reversed when the numbers relating to the primary stage are replaced by those characteristic of the third stage.

H. M. D.

**The Adsorptive Power of the Hydroxides of Silicon, Aluminium, and Iron.** VI. PAUL ROMANO (*Zeitsch. anorg. Chem.*, 1912, **80**, 174—175. Compare A., 1912, ii, 1145).—The colloids of clay have very little adsorptive power for azo-dyes, and the colouring matter of unknown constitution which is present in the waste water from sulphite cellulose is not adsorbed.

C. H. D.

**Adsorption.** VIII. **Adsorption by Starch in Mixed Solutions.** ADAM V. RAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1912, **45**, 7—12. Compare this vol., ii, 114).—The author has investigated the adsorption by starch of alkali in presence of salts and of two alkalis simultaneously.

Potassium and sodium salts of organic and inorganic acids cause considerable increase in the amount of sodium hydroxide adsorbed by starch, the carbonates being appreciably less effective than the other salts; the extent of the adsorption increases continuously with the concentration of the salt. The adsorption of the large proportions of alkali thus occurring is not accompanied by appreciable gelatinisation of the starch.

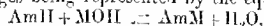
Barium salts exert a similar influence on the adsorption of barium hydroxide by starch, but the small amount of ammonium hydroxide adsorbed by starch is scarcely affected by the presence of ammonium salts. A more complicated course is followed by the adsorption when the hydroxide and salt possess dissimilar cations. The systems  $\text{NaOH} : \frac{1}{2}\text{BaCl}_2$  and  $\frac{1}{2}\text{Ba(OH)}_2 + \text{NaCl}$  give identical results.

With the system  $\text{Ba(OH)}_2 + \text{NaOH}$  both alkalis are adsorbed, the former to a higher and the latter to a lower extent than when present alone, so that the adsorption of barium ions is raised and that of sodium ions diminished by excess of hydroxyl ions.

Ammonium hydroxide is practically without influence on the adsorption of sodium or barium hydroxide.

T. M. P.

**Adsorption. IX. Adsorption and Hydrolysis.** ADAM V. RAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 13—21).—The assumption is made that the action of alkali on starch yields "starchates" or chemical compounds analogous to alkoxides and acetates. Since starch adsorbs both alkali and water simultaneously, in the solid phase hydrolytic decomposition of the starchate would occur, these changes being represented by the equation:



where AmH indicates starch and AmM the starchate.

If the initial concentration of the alkali is  $a$  milli-equivalents in volume  $v$ , and the weight of starch  $m$  grams or  $1000m/162.08a$  or  $\lambda$  milli-equivalents, and if, further, after the establishment of equilibrium, there are present  $x$  milli-equivalents of starchate,  $N-x$  of free starch and  $a-x$  of free alkali, then  $x/(N-x)(a-x) = k_n$  should give constant values. The index  $n$  of the constant represents the number of  $\text{C}_6\text{H}_{10}\text{O}_5$  groups present in the given starchate per equivalent of metal.

With potato and St. Vincent and Bermuda arrowroot starches constant values are obtained with lithium, sodium, and potassium hydroxides for  $k_n$  if  $n = 3$ . In the case of starches with small granules, such as rice starch, the constancy is less satisfactory, and with wheat starch constant values are obtained for  $k_4$ . The starchates formed by the two latter starches hence differ in type from those given by potato and arrowroot starches.

With barium, strontium, and calcium hydroxides, less concordant numbers are obtained, but these are in fairly good agreement with the value  $n = 1$ .

The constancy of the values of  $k$ , the negligible influence of change of temperature on the adsorption of alkali hydroxides by starch, and the intensification of the adsorption in presence of salts (compare preceding abstract), render highly probable the existence of starchates. T. II. P.

**Influence of the Geometric Form of Solids on the Chemical Reactions which they Undergo.** G. REBOUL (*Compt. rend.*, 1913, **156**, 548—550. Compare *ibid.*, 1912, **155**, 1227).—The author has measured any change of rate of attack of a gas on a solid, by varying the curvature of the solid, in such cases as the action of iodine vapour on silver, and finds that, either at the ordinary pressure or under reduced pressure, the action of the gas on the solid is most rapid at those points where the mean curvature is the greatest, and explains the phenomenon on the grounds of capillarity, the gaseous concentration being greatest at the points where the radius of curvature is least. W. G.

**Capillary Phenomena in Gases. Extension of Laplace's Formula to the Contact Solid-gas.** G. REBOUL (*Compt. rend.*, 1913, **156**, 688—691).—Working with copper cylinders of different diameter, subjected to the gas from vulcanised caoutchouc, the author shows that the amount of copper compound formed is given by  $at = k_1 \frac{1}{r} + c$ , where  $q$  is the thickness of the layer of copper

compound formed,  $R$  the radius of the cylinder, and  $a$ ,  $b$ ,  $c$  three constants varying slightly with the pressure of the vapour. Assuming that there is an increase in the concentration of the gas at the surface of the metal, he obtains  $a^2 = kT + c$ , where  $P$  is the concentration of the reacting gas, which is thus a linear function of  $1/P$ ; thus there is at each point of the surface of separation of solid gas an excess of pressure proportional to the mean curvature, and so Laplace's formula holds good for such cases. W. G.

**The Differential Tonometry of Solutions and the Theory of Arrhenius.** EUGENE FOUARD (*Compt. rend.*, 1913, 156, 622-625, Compare A., 1911, ii, 267, 1071; 1912, ii, 436).—A photograph and description is given of a tonometer, in which the author has made determinations on equimolecular solutions of potassium chloride and sucrose, and has obtained results which are in agreement with his measurements of osmotic pressure (*loc. cit.*), and thus opposed to the ionic theory of solution. W. G.

[Stratified Systems.] RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 74-77).—It is shown that the experiments described by Hatschek (A., 1912, ii, 439) cannot be accepted as disproving Ostwald's view that the formation of stratified layers of insoluble substances as a result of slow diffusion in jellies is due to the intervention of supersaturation phenomena.

The slow interaction of copper nitrate and sodium carbonate, which occurs when silicic acid jellies containing the two substances are brought into contact, has been found to give rise to irregularly stratified precipitation layers of basic copper carbonate, the structure of which resembles closely that shown by certain malachites.

II. M. D.

**New Apparatus for Quantitative Dialysis.** A. GOLDBERG (*Chem. Zeit.*, 1913, 37, 259-260).—In order to dialyse a substance exhaustively, using a small volume of water, the material is enclosed in a suitable membrane, which is so placed in a modified Soxhlet apparatus that it presents as large a surface as possible to the water. Should it not be advisable to heat the product above 50° a capillary tube may be attached and ebullition maintained under reduced pressure. J. C. W.

**Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures.** 1. PAUL PASCAL and LÉON NOBLET (*Bull. Soc. chim.*, 1913, [iv], 13, 151-161).—This is the first of a series of papers in which the authors propose to deal with binary mixtures of compounds of the type  $R \propto \beta - R'$ , where  $R$  and  $R'$  are aromatic nuclei and  $\alpha$  and  $\beta$  may be  $\cdot\text{CH}_3$ ,  $\cdot\text{CH}_2$ ,  $\cdot\text{C}_2$ ,  $\cdot\text{NH}$ ,  $\cdot\text{N}$ , or  $\cdot\text{O}$ . Such investigations have been made already by Beck (A., 1901, ii, 616) and by Bruni (A., 1912, ii, 1013). The authors propose to ascertain (1) whether "mixed crystals" are formed, and if so, over what range of temperature, and (2) what relationship exists between the structures of the two components and the

property of simultaneous crystallisation. The mixtures now examined are: (1) stilbene with (*a*) dibenzyl, (*b*) toluene, (*c*) azobenzene, (*d*) hydrazobenzene; (2) toluene with (*a*) dibenzyl, (*b*) azobenzene, (*c*) hydrazobenzene; (3) dibenzyl with (*a*) hydrazobenzene, (*b*) azobenzene; and (4) azobenzene with hydrazobenzene. Tables and graphs showing the fusion curves of these mixtures are given. They show that compounds of the type  $R-\alpha-\alpha-R$  taken two at a time give a continuous series of mixed crystals, and are probably strictly isomorphous, although there are shades in this isomorphism, thus: in the case of a binary mixture of two compounds having the same multivalent central atoms, or the same central linkings, the fusion curve generally shows no minimal point, whilst a minimal point develops more and more clearly as differences in the two constitutional characters mentioned become more noticeable, and is most marked in a mixture of hydrazobenzene,  $NHPh \cdot NHPh$ , and toluene,  $CPh \cdot CPh$ . Further, hydrazobenzene shows an unforeseen tendency to produce minimal points on the curves, possibly owing to the ease with which its  $\cdot N \cdot$  atoms may become quinquivalent.

T. A. II.

**Chemical and Crystal Molecules.** EVERETT S. FEDOROV (*Zeitsch. Krist. Min.*, 1913, 52, 22—43).—Several examples are quoted from the author's tables (A., 1912, ii, 772). In considering the symmetry relations of the chemical molecule the arrangement of the peripherically placed radicles must be taken into account in addition to the nucleus itself. As a rule, the symmetry relations shown by the crystal cannot be expressed by the chemical molecule alone, and two or more of these must be united to form the crystal molecule.

L. J. S.

**Formation of Crystal Faces.** A. BERTHOUD (*J. Chim. phys.*, 1902, 10, 624—635).—According to Curie, crystals take the habit which gives them the minimum of superficial energy, so that the relative areas of the faces depend on their capillary constants. A crystal departing from the equilibrium shape when placed in a solution of suitable strength should dissolve from some faces and grow on others.

Actually the differences of solubility in crystals are so minute as to be without influence on their crystalline habit in comparison with the effect of different rates of crystallisation along different axes. Taking the surface energy of two faces of a crystal in its normal habit as of the order 100 and 800 ergs per sq. cm. respectively (Hillelt), the author calculates that even in crystals departing very considerably from the normal habit an appreciable difference in solubility can only arise when the dimensions are microscopic. Surface energy might come into play in extreme cases, as, for example, in preventing a substance from crystallising in thin plates when normally it crystallises in slender needles.

The main factors which influence crystalline habit are the internal structure of the crystals and the degree of supersaturation and the nature of the concentration and other currents in the solution



during deposition. According to Noyes and Whitney (1897), the dissolution of a crystal is governed by the rate of diffusion of the dissolved molecules across the zone of falling concentration which, being replenished instantaneously from the crystal, remains saturated on one side. Le Blanc has applied this theory to the reverse process of crystallisation. The author agrees with Wagner that Le Blanc's theory fails to account for the varying rates of crystal growth on different faces. Wagner suggests that the thickness  $\delta$  of the diffusion zone varies from one face to another, but  $\delta$  being at least 0.03 mm. with the most violent agitation (Brunner), is not likely to be influenced by forces of molecular magnitude at the crystal surface.

The rate at which equilibrium tends to establish itself between a given area of crystal surface  $S$  and the solution is proportional to the difference in the concentration of the saturated solution  $c_0$  and the solution in immediate contact with the crystal  $c'$ . Thus,  $dx/dt = kS(c' - c_0) = SD(c - c_0)/(\delta + D/k)$ , where  $k$  is the velocity constant of crystallisation of the given surface,  $D$  the diffusion constant, and  $c$  the mean concentration in the diffusion zone. This formula reduces to that of Noyes and Whitney when  $D/k$  is very small in comparison with  $\delta$ , that is, when the solution is absolutely still. The more nearly this condition is attained in practice the more nearly the crystal faces approximate to equal rates of growth, and facets may then appear which are not seen when the solution has been agitated.

R. J. C.

**Chemical Analogies of Substances Showing a Crystallographic Relation to Potassium Sulphate.** EUGRAF S. EDEGBO (Zeitsch. Kryst. Min., 1913, 52, 11-21).—A variety of substances of the hypohexagonal type having nearly the same symbols as potassium sulphate fall together in the author's tables (A., 1912, ii, 772), for example,  $\text{SO}_4\text{K}_2$ ,  $\text{BeF}_4(\text{NH}_4)_2$ ,  $\text{HgBr}_2\text{Cs}_2$ ,  $\text{ZnCl}_2\text{K}_2$ ,  $\text{CuCl}_2(\text{NMe}_3)_2$ , etc. These exhibit the same type of chemical formula (although the numbers of atoms and the valencies differ); and they are described as isotectonic substances, and their crystals as isogonal.

L. J. S.

**Efflorescence of Crystals under Water.** MORRIS FORT (Chem. News, 1913, 107, 86).—If slightly effloresced crystals of sodium sulphite,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , are placed in an excess of water in a test-tube, the opaque outer crust dissolves, and the crystals become clean and bright. On gently warming, the crystals rapidly become opaque and powdered in appearance, and analysis shows them to have effloresced to a considerable extent. The author considers that the best explanation is that dehydration of the crystals, due to rise in temperature, takes place faster than solution can be effected.

T. S. P.

**Liquid Crystals of Ammonium Oleate.** A. MLODZIEGOSKI (Zeitsch. Kryst. Min., 1913, 52, 1-10).—The so-called liquid crystal of ammonium oleate may be obtained by the evaporation at the

ordinary temperature of a solution in water and alcohol. They are only formed in the presence of water or at a sufficiently high temperature, and by the addition of more water they exhibit myelin forms. The conclusion is drawn that the structure observed is of the nature of an emulsion rather than that of liquid crystals (compare A., 1912, ii, 109).

L. J. S.

**Nature of the Electrical Synthesis of Colloids.** CARL BENEDICKS (*Koll. Chem. Beihefte*, 1913, 4, 229—260. Compare Kutscherov, A., 1912, ii, 1148; Benedicks, this vol., ii, 99).—The microstructural changes which are exhibited by the surfaces of the electrodes after electrical disintegration have been investigated with the object of throwing light on the nature of the disintegration process. The apparatus employed was practically identical with that described by Svedberg, ethyl ether being used as dispersive medium, and the current passed between electrodes of various metals and alloys.

The results obtained indicate that the process is essentially thermo-mechanical. When the conditions are such that arc discharge takes place for a very short time interval, as may easily be arranged if the current is furnished by an induction coil and a Leyden jar is placed in parallel with the discharge gap, it is found that the surfaces of the electrodes exhibit well-formed, eruptive craters, which are attributed to the melting of the metal under the influence of the discharge. When the discharge ceases, the surrounding liquid comes in contact with the hot metal, and this is supposed to be directly responsible for the disintegration of the electrodes. In support of this view it has been found that exactly similar crater-like structures can be obtained when a gentle current of hot air is allowed to impinge on the surface of a highly viscous substance, such as asphalt.

In accordance with the thermo-mechanical nature of the process, the most important factors in connexion with the electrical disintegration process are the latent heat of liquefaction and the thermal conductivity of the disintegrating metal.

Ultra-microscopic observations, made with the colloidal metal solutions obtained by Svedberg's method, have shown that the particles are spherical, the diameter varying over a wide range with an upper limit of about  $5\mu$ .

H. M. D.

[Preparation of a Dispersoid Solution of any Substance.]

P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1913, 4, 175—191).—A theoretical paper in which the author discusses the conditions under which it is possible to obtain any substance in the form of a dispersoid solution.

H. M. D.

**Physical Properties of Colloidal Solutions.** JOSEF FRANK (*Koll. Chem. Beihefte*, 1913, 4, 195—228).—Measurements have been made of the volume changes which accompany the absorption of water by colloids, of the heat of liquefaction, and the coefficient expansion of various colloids, and also of the viscosity of certain colloidal solutions.

The absorption of water by gelatin or starch and of colophony

by oil of turpentine is attended by contraction, the magnitude of which, when referred to unit volume of the gelatin, starch, or oil of turpentine, is independent of the composition of the mixture. The transition from the solid to the liquid state shows no appreciable absorption of heat according to experiments with colophony, mixtures of colophony and oil of turpentine, and mixtures of gelatin and water. The coefficient of expansion of gelatin water mixtures increases with rise of temperature to a maximum, afterwards falling to a minimum, and at still higher temperatures increasing again. The maxima and minima become more sharply defined as the proportion of gelatin in the mixture increases, and at the same time the temperatures at which they occur are found to rise. In the case of colophony and its mixtures with oil of turpentine, the coefficient of expansion rises with the temperature, at first quickly, then more slowly, and later again more rapidly. As the proportion of oil of turpentine in the mixture increases, the coefficient of expansion becomes greater, but the rate at which the coefficient increases with temperature becomes less.

From the examination of a large number of colloidal solutions of dyes, dissolved in water and alcohol, it has been found that the effect of the dye on the viscosity is in general greater for alcoholic than for aqueous solutions. The viscosity of solutions of malachite-green and safranine was found to vary with time. H. M. D.

**Thermo-chemical Researches on Solution and their Bearing on Theoretical Considerations concerning the Relations between the Chemical Properties of Solutions.** NICOLAS A. KOLOSOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 22—52. Compare this vol., ii, 22).—On the assumption that the change of any property for mixtures or chemical compounds is an external manifestation of the action of chemical affinity, it may be asserted that, in the case of aqueous solutions of electrolytes, the divergence of any property from the mean of those of the solvent and solute is a consequence of the formation of hydrates. Assuming, further, the formation of hydrates of the ions, all such divergences must necessarily follow an additive law.

In order to ascertain the limits of applicability and a measure of the general character of this proposition, the author examines the relations between the values obtained, for various salts, of (1) the lowering ( $\Gamma$ ) of the coefficient of distribution of acetic acid between water and ether under the influence of 1 gram equivalent of dissolved salt (compare A., 1911, ii, 591, 705); (2) the change ( $\Gamma'$ ) in the temperature of separation of an aqueous solution of isobutyric acid produced by a half gram-equivalent of dissolved salt (compare Smirnov, A., 1907, ii, 334); (3) the change ( $\Gamma''$ ) in the absorbability of carbon dioxide by water caused by one gram equivalent of dissolved salt (compare Sotchenov, A., 1875, 261, 1159; *J. Russ. Phys. Chem. Soc.*, 1886, 18, and 1887, 19). The constancy exhibited by the two ratios,  $\Gamma'/\Gamma - K'$  and  $\Gamma''/\Gamma - K''$ , is regarded as evidence of the chemical nature of these properties.

and *Bull. Acad. roy. Belg.*, 1913, 56—67.

With other properties, such as density, capillarity, etc., no such simple relations were obtained.

Measurements have been made of the heats of solution and specific heats of sodium and potassium chlorides and nitrates in water and in various mixtures of water and ethyl alcohol. In each of these solvents the differences between the heats of solution of (1) sodium and potassium nitrates, and (2) sodium and potassium chlorides are very nearly equal. Approximate equality is also exhibited between the differences for (1) potassium chloride and nitrate, and (2) sodium chloride and nitrate.

T. H. P.

**Influence of Temperature on the Velocity of Chemical Reactions.** A. BARNHOLD (*J. Chim. phys.*, 1912, 10, 573-597).—According to Arrhenius' theory, the "active part" in chemical change is formed reversibly in accordance with van't Hoff's equation for static equilibrium. The active part is supposed to be transformed chemically at a definite rate in accordance with the law of mass action. If  $k'$  is the rate of formation of the active part and  $k''$  of the reverse action, and  $k$  the rate of chemical transformation of the active part, the concentration  $C$  of the latter is proportional to  $k'/(k+k'')$ . It is not permissible to assume with Arrhenius that  $k$  is independent of temperature.

The modification of Arrhenius' theory put forward by Trautz (A., 1911, ii, 381), in which the active part consists of molecules undergoing a preliminary dissociation, is open to a similar objection, as also is the additive compound hypothesis. According to Goldschmidt (A., 1909, ii, 390), only those molecules react the velocity of which exceeds a certain minimum. The author proposes a modification of this theory, in which velocity is replaced by "energy of internal atomic vibration." Those molecules the atoms of which are in an unstable configuration or are vibrating beyond a certain critical amplitude constitute the "active part." In gaseous actions other than intramolecular actions, it is necessary to assume that transient additive compounds are formed which are dissociated again into the original constituents or into new constituents according to their content of energy or their configuration.

The ordinary temperature-equation is modified by the addition of a new factor,  $f(T)$ , and thus becomes  $\log k' - k'' = A/T + B/\log T + (T + D)/f(T)$ . The new term  $f(T)$  is intended to take account of the effect on  $k$  of various factors, such as the increase in the proportion of active molecules exceeding the critical energy, the increase in the average energy of the molecules which exceed the critical energy, and, in the case of solutions, the viscosity. In practice,  $f(T)$  is usually negligible in comparison with experimental errors.

R. J. C.

**Action of Low Temperatures on Explosives.** ANDRÉ KLING and DANIEL FLORENTIN (*Compt. rend.*, 1913, 156, 624-626).—A study of the influence of cooling on the sensitiveness of different explosives, on the force and rate of their explosions, comparison being made between results obtained at the ordinary temperature and

at  $-190^{\circ}$  (liquid nitrogen). The sensitiveness to percussion is considerably diminished at low temperatures, the cooling effect being shown both by the detonator and the explosive itself. The force of the explosion does not appear to be diminished by cooling, providing that the percussion is sufficiently powerful to produce total deflagration of the explosive. When detonation occurs, the propagation of the explosion wave is not affected by cooling.

W. G.

**The Oxidation of Complex Cobalto-organic Compounds** H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1913, 156, 625—627).—A study of the rate of oxidation of solutions containing a cobalt salt and either glycerol or lactic acid, to which an excess of alkali hydroxide has been added, the amount of oxygen fixed by the cobalt in a given time being determined. The reaction is unimolecular, and the value of the constant  $K$  is independent of the concentration of the cobalt salt, but decreases rapidly with increase in concentration of the alkali. The author considers that the mechanism of the oxidation is similar to that in the case of the cobaltocyanides (compare Manchot and Herzog, A., 1901, ii, 549).

W. G.

**Velocity of the Reaction between Sodium Thiosulphate and Sodium Bromoacetate.** SERGIUS KRAPIVIN (*Zeitsch. physikal. Chem.*, 1913, 82, 439—447).—The velocity of the reaction between sodium thiosulphate and sodium bromoacetate is determined by the same method as that employed for determining the velocity between sodium thiosulphate and chloroacetate (A., 1912, ii, 926). The reaction is bimolecular, the velocity constant depending on the concentration; for 0.25*N*-solutions  $k=1.605$ ; 0.05*N*-solutions  $k=0.697$ , and for 0.01*N*-solutions  $k=0.456$ . Doubling the concentration of either the bromoacetate or the thiosulphate brings about the same change in the velocity constant. The addition of 0.01*N*-sodium bromide, sodium iodide, sodium nitrate, or sodium sulphate effects the velocity constant to the same extent as the addition of the same quantity of either sodium thiosulphate or sodium bromoacetate. The addition of alcohol to the reaction mixture causes an increase in the velocity constant.

J. F. S.

**Hydrolysis of Metallic Alkyl Sulphates.** GEORGE A. LINHALL (*Amer. J. Sci.*, 1913, [iv], 35, 283—289. Compare A., 1912, ii, 927).—The rate of saponification of sodium ethyl sulphate by sodium hydroxide and of barium methyl sulphate and strontium methyl sulphate by barium hydroxide has been examined in aqueous solution at  $60^{\circ}$ . The data indicate that the reaction proceeds in all three cases in accordance with the equation for a bimolecular change. This result differs completely from that obtained in similar experiments by Kremann (A., 1910, ii, 596), and the author draws the conclusion that Kremann's data are untrustworthy, and that the interpretation of the results is consequently without foundation.

H. M. D.

**Re-investigation of the Velocity of Sugar Hydrolysis. II. The Role of Water.** MARTIN A. ROSASOFF and H. M. POTTER (*J. Amer. Chem. Soc.*, 1913, **35**, 248-258). In an earlier paper (A., 1912, ii, 34) it was shown that the hydrolysis of sucrose is a strictly unimolecular reaction.

Various explanations, including those of Cohen (A., 1897, ii, 481) and Arrhenius (A., 1899, ii, 359), have been offered for the fact that the velocity of hydrolysis of sucrose is a function of the initial concentration, but it is now shown that none of these is adequate. A new theory is therefore proposed, which states that water plays a double rôle in the reaction: (1) it takes part in the reaction, and contributes to its velocity in accordance with the law of mass-action, and (2) it acts as a negative catalyst by its dissociating power. In accordance with this view, the mechanism of sucrose hydrolysis appears to depend on the existence of a molecular complex, the concentration of which determines the velocity of the reaction. Water retards the reaction by dissociating this complex.

E. G.

**Action of Neutral Salts on Bleaching Solution.** SYDNEY H. HIGGINS (*J. Soc. Dyers*, 1913, **29**, 85-89).—See P., 1912, 28 130.

H. M. D.

**Neutral Salt Reactions. II. A Double Neutral Salt Reaction and the Action of Glauber's Salt on Wool.** MORRIS FORT (*J. Soc. Dyers*, 1913, **29**, 80-85. Compare A., 1912, ii, 1047).

According to the views brought forward in the previous paper, salts which do not give an alkaline reaction with litmus or alizarin should exhibit alkalinity when more strongly acid indicators are added to the boiling solutions. In support of this it has been found that a hot solution of sodium chloride, which is inactive towards alizarin, gives a feeble alkaline reaction with nitroalizarin and a distinctly alkaline reaction with dinitroanthrachrysone sulphonic acid.

Although no alkalinity is indicated on the addition of alizarin to boiling solutions of either sodium chloride or calcium sulphate, yet when the solutions are mixed, an alkaline reaction is immediately developed. This is attributed to double decomposition, sodium sulphate being formed in sufficient quantity to give the alizarin reaction.

The action of aqueous solutions of sodium sulphate on wool has been investigated with reference to its tensile strength and dyeing properties, and the results are supposed to show that the basic properties of wool enable it to react with sodium sulphate in boiling solution in much the same way as other organic bases. Neutral salt reactions are considered to play a part in other technical processes and also in physiological changes. H. M. D.

**Colour Changes Among Dyes of the Triphenylmethane Series as Influenced by the Hydrogen Ion Concentration of Acids of Different Dissociation Constants.** HENRY C. BIDDLE (*J. Amer. Chem. Soc.*, 1913, **35**, 273-281. Compare A., 1912, i, 296; ii, 1048). A study of the conversion of the benzenoid forms of

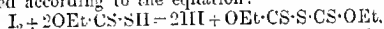
certain dyes of the triphenylmethane series into the quinonoid forms by acids of different dissociation constants has shown that there is a marked similarity between the action of the acids in this case and their catalysing influence in the case of the cinchona alkaloids.

The rate of development of colour in a solution of magenta in sulphurous acid to which a little formaldehyde has been added increases in equivalent solutions with acids of decreasing dissociation constant, and is retarded by acids of increasing dissociation constant. The reaction forms a useful lecture experiment for demonstrating the accelerating catalytic action of the slightly dissociated organic acids and the inhibiting action of the highly ionised mineral acids. The velocity of the reaction appears also to increase with the molecular concentration of an organic acid.

The action of excess of an acid on a rosaniline dye or its carbinol base leads to an equilibrium between the coloured and colourless forms which is largely dependent on the concentration of the hydrogen ions of the acid. The velocity of the reaction in the case of methyl-violet with acetic or chloroacetic acid seems to increase with the decreasing dissociation constant of the acid. E. G.

#### Xanthic Acid and the Kinetics of its Decomposition.

HANS VON HALBAN and ALEXANDER KIRSCH (*Zeitsch. physikal. Chem.*, 1913, **82**, 325—360).—Xanthic acid usually decomposes violently in several minutes after preparation. It is shown that this is due to autocatalysis, in which the alcohol, formed as a product of the decomposition, is the catalyst. The authors show that if xanthic acid is intimately mixed with phosphoric oxide it becomes stable, and can be kept for weeks. The rate of decomposition of the acid is determined in solutions in benzene, chloroform, carbon disulphide, light petroleum (b. p. 65—80°), ether, nitrobenzene, acetone, and alcohol at temperatures 0°, 4.7°, 25°, 45°, 65°, and 80°. The course of the reaction is followed by titrating portions of the solution with a standard iodine solution when the undecomposed acid can be estimated according to the equation:



The velocity of decomposition, in solutions where the decomposition is rapid, is in accordance with a reaction of the unimolecular type, but for those solutions in which the reaction is relatively slow the constant, calculated by the equation for unimolecular reactions, gradually increases, thus pointing to an autocatalysis. The velocity constant varies enormously in the different solvents; thus, if at 25° the constant for ethyl alcohol is 1,000,000, acetone gives 25,950, ether 485, nitrobenzene 315, benzene 5.15, chloroform 3.64, light petroleum 1.59, and carbon disulphide 1.0. It is shown that there is no connexion between the dielectric constants of the solvents and the velocity of the reactions. The effect of adding quantities of various substances to the various solutions is also investigated. The addition of alcohol to the benzene solutions causes an increase in the velocity of the reaction. The addition of many other substances causes a similar increase; thus the constant for a pure benzene

solution at  $25^{\circ}$  is 0.0000068 for a 0.01 normal solution of xanthic acid; if the following substances are added in quantities sufficient to form a 0.2 normal solution, the following values are obtained: methyl alcohol, 0.0028; ethyl alcohol, 0.0036; propyl alcohol, 0.0023; acetic acid, 0.00021; acetone, 0.000075; tribromophenol, 0.000015; triphenylcarbinol, 0.000031. In ethereal solution sulphuric acid causes a considerable increase in the velocity, whereas acetic acid and hydrochloric acid increase it to the same extent, which is, however, much less than with sulphuric acid. The temperature-coefficient of the reaction is much smaller than that usual for unimolecular reactions; it conforms well with the formula of Arrhenius. The molecular weight of xanthic acid was determined in solutions of benzene and carbon disulphide, and shown to be normal.

J. F. S.

**Structure of Some of the Elements.** HAWKSWORTH COLLINS (*Chem. News*, 1913, 107, 99—100).—Reference is made to the advertisement columns of *Nature* and *Chem. News*, 1906, for priority of the idea that "the acidity or non-metallic nature of an element is always due to a pair or pairs of electro-positive forces, each pair emanating from a portion of the element" of mass 4. Eleven pairs of elements are cited, differing in mass by four units and in valency by two units, such as phosphorus and aluminium, aluminium and sodium, etc. The combination of oxygen and helium to form neon is cited in support of these views of atomic structure.

F. S.

**Twentieth Annual Report of the Committee on Atomic Weights.** Determinations published during 1912. FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1913, 35, 227—225).—A summary of the atomic-weight investigations carried out during 1912 and the results obtained.

E. G.

**A New Source of Error in the Determination of Atomic Weights.** ICULIO GUARIESCHI (*Atti R. Accad. Sci. Torino*, 1913, 48, 128—131).—Applying his reaction for the detection of bromine (A., 1912, ii, 989, and this vol., ii, 333), the author has been unable to find chlorides which do not contain bromides, or chlorates or iodates free from bromates. From preliminary colorimetric determinations it is probable that even the purest potassium chlorate contains bromate to the extent of one or two parts in ten thousand. This would be enough to cause perceptible error in atomic weights involving an analysis of these substances.

R. V. S.

**The Development of Avogadro's Theory.** CARL GRAFIC (*J. pr. Chem.*, 1913, [ii], 87, 145—208).—Historical. The author traces the position and development of the above theory from the time of its advancement in 1811 until its general acceptance more than fifty years afterwards.

F. B.

**What are Bases and Acids?** RICHARD MEYER (*J. pr. Chem.*, 1913, [ii], 87, 280—286).—A criticism of Vorländer's definitions (this vol., i, 130).

F. B.



**Gas Generator.** FRANK SOUTHERDEN (*Chem. News*, 1913, 107, 86).—The apparatus has been designed more especially for the generation of hydrogen sulphide. The ferrous sulphide is contained in a tower, fitted at the top with a delivery tube and stop-cock; the constriction in the lower part of the tower contains a radially grooved plug, so that a drainage chamber is formed underneath. The side-tube from this drainage chamber is connected with a side-tube opening into the upper part of the acid reservoir, with the result that the dense stale liquor tends to sink in the reservoir as returned, relatively fresh acid being available on re-starting.

T. S. P.

**A Reflux Condenser.** S. W. WILEY (*J. Ind. Eng. Chem.*, 1913, 5, 151).—The apparatus consists of tubes of block tin connected with bell-shaped condensers of spun copper. The bell is composed of two sections, which are separated by a perforated partition. The bell is surrounded by cold water, and condensation takes place on the upper surface of the bell. The condenser is very efficient, and can be used for ether extractions.

T. S. P.

**A New Form of Laboratory Extraction Apparatus.** A. F. PERKINS (*J. Ind. Eng. Chem.*, 1913, 5, 148–149).—The apparatus consists essentially of an extraction flask with a long neck, which is constricted at the base. The flask is flat-bottomed, and has a diameter of  $2\frac{3}{4}$  inches, and a height of 2 inches to the base of the neck. The constriction is about half an inch in diameter as well as in height, and the neck above the constriction is 12 inches long by  $1\frac{1}{2}$  inches in diameter. A tube through which cold water flows fits into the upper part of the neck, and acts as a condenser. The extraction thimble fits on to the constriction at the base of the neck.

The apparatus is much simpler than the ordinary extraction apparatus, and rapid and complete extractions can be carried out.

T. S. P.

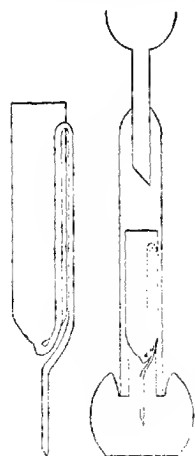


FIG. I

FIG. II

**A Modified Extraction Apparatus.** G. M. MACNIDER (*J. Ind. Eng. Chem.*, 1913, 5, 150–151).—The apparatus combines the best features of the Soxhlet and Knorr extractors, a small siphon extraction tube of the Soxhlet type fitting into a Knorr adapter. The principle is readily understood from the accompanying diagrams.

T. S. P.

**A Useful Valve.** NATHAN SMITH (*J. Ind. Eng. Chem.*, 1913, 5, 235).—The valve is placed between the desiccator and the safety bottle

when using a water-pump. A piece of glass tubing, drawn out evenly at one end (the delivery tube of a pipette answers very well), is fitted with a piece of rubber, which acts as a valve. A piece of wire is drawn through the centre of the rubber, and then coiled into a spiral outside the tube, so that the rubber is allowed some play, but cannot be sucked back right up the tube. Another piece of glass tubing is then fitted over the valve tube by means of a collar of rubber tubing, and connects with the desiccator.

T. S. P.

**New Separating Funnel.** C. E. PARKER (*J. Amer. Chem. Soc.*, 1913, **35**, 295--297).—In order to overcome the difficulty due to the formation of persistent emulsions, which are often produced when animal or vegetable extracts are shaken with immiscible solvents, a special form of separating funnel has been devised. The separators are of flat shape, and are held in a horizontal position during the extraction and in a vertical position when the contents are to be withdrawn. The advantage of this form is that the liquids are distributed in thin layers over a large area, so that the contiguous surfaces are from eight to ten times as great as with the same amounts of liquid in separators of the ordinary kind. A gentle movement of the liquids in contact with one another can be effected by means of a nearly horizontal disk making 20 revolutions per minute. The separators lying on the rotating disk are tilted about gently in such a way that no actual mixing of the liquids takes place.

E. G.

## Inorganic Chemistry.

**Physico-chemical Studies on Tellurium.** I. ERNST COHEN and J. F. KROXER (*Zeitsch. physikal. Chem.*, 1913, **82**, 587--611).—An account is given of the older investigations on tellurium. By means of density determinations it is shown that tellurium exists in two forms,  $Te_\alpha$  and  $Te_\beta$ , which are present as dynamic allotropes in equilibrium  $Te_\alpha \rightleftharpoons Te_\beta$ . The equilibrium amounts are changed by change in temperature. It is shown that the treatment to which tellurium has been subjected influences the density in a marked degree. The density varies between 6.272 and 5.949, depending on the temperature. Some tellurium, prepared by the reduction of telluric acid by means of hydrazine sulphate, was found to have a density 3.242. The low value is shown to be due to the absorption of large volumes of nitrogen. The authors state that with the exception of the atomic weight, all physico-chemical constants of tellurium are to be doubted on account of the existence of the two forms of tellurium existing in unknown proportions in all specimens of tellurium.

J. F. S.

**After-Luminosity in Pure Nitrogen after the Passage of Electric Discharge.** A. KOENIG and E. ELÖN (*Physikal. Zeitsch.*, 1913, **14**, 165—167).—From observations on the after-luminosity effect which is exhibited when a current of nitrogen is passed through a discharge tube (Strutt, A., 1912, ii, 153, 477, 935), the authors have obtained evidence in support of Strutt's view that the effect is due to the formation of an active modification of nitrogen. The opinion has been recently expressed by Comte (this vol., ii, 210) that the after-luminosity is dependent on the presence of small quantities of oxygen in the nitrogen, but this is not in agreement with the authors' results.

The nitrogen employed contained argon, 1.5% of carbon dioxide, and traces of oxygen. It was freed from carbon dioxide by means of potassium hydroxide, dried over calcium chloride, freed from oxygen by passing over heated copper, and then completely dried by passing through a spiral tube cooled to  $-80^{\circ}$ .

The intensity and duration of the after-effect depend on the pressure of the gas. As the pressure falls, the duration of the after-effect increases. At very low pressures the luminosity can only be observed readily if the thickness of the layer of gas is sufficiently large. The addition of small quantities of oxygen appears to lessen the intensity and duration of the effect, and hydrocarbons have a similar influence. Traces of hydrocarbons, which can scarcely be recognised in the spectrum of the discharge tube, have an appreciable influence on the after-luminosity. The colour changes to red or violet-red, and the bands attributable to active nitrogen are almost completely extinguished by the cyanogen spectrum.

H. M. D.

**The Chemically Active Modification of Nitrogen.** (Holl.) ROBERT J. STRUTT (*Physikal. Zeitsch.*, 1913, **14**, 215).—In reply to Comte (this vol., ii, 210), who attributes the after-luminosity accompanying the jar discharge through nitrogen to the presence of small quantities of oxygen, the author points out that the effect in question is obtained with nitrogen, which shows no trace of cloud formation in contact with phosphorus. In regard to the sensitiveness of this test for oxygen, it has been found that the addition of the one hundred-thousandth part of oxygen to non-reactive nitrogen is sufficient to produce the cloud effect. If the nitrogen, purified by contact with a fresh surface of phosphorus, is passed over a long column of copper gauze at a red heat, the after-luminosity effect remains unchanged. If the nitrogen is passed through a tube containing copper gauze which is cooled to  $-190^{\circ}$ , the after-luminosity becomes intensified, and this is attributed to the removal of traces of condensible impurities.

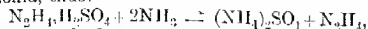
H. M. D.

**Extraction with Liquefied Gases and the Ammonolysis of Hydrazine Sulphate.** FRITZ FIEDRICHUS (*J. Amer. Chem. Soc.*, 1913, **35**, 244—247\*).—Apparatus has been devised for carrying out extractions with liquefied gases as solvents. The extraction apparatus is a modification of the Landsiedl form (A., 1902, ii, 390), and

\* and *Zeitsch. anorg. Chem.*, 1913, **26**, 201—203.

the condenser is of the screw type; both are enclosed in vacuum jackets.

The apparatus has been found of considerable service in a study of the ammonolysis of hydrazine sulphate. Browne and Welsh (A., 1911, ii, 1084) have shown that this salt is decomposed by liquid ammonia, thus:



and have suggested that as ammonium sulphate is insoluble in liquid ammonia, whilst hydrazine is soluble, the reaction might be useful for the preparation of anhydrous hydrazine. It has now been found that the ammonolysis proceeds quantitatively, and that a yield of 90–95% of hydrazine can be obtained; it is considered that the base could be readily prepared in large quantities by this method if the apparatus were constructed of iron instead of glass.

E. G.

**Chemistry of the Formation of Nitric Oxide in the High Tension Arc.** II. FRANZ FISCHER and ERL HERN (*Ber.*, 1913, 46, 603–617).—Details are given of the apparatus and methods used to obtain the results described in a previous paper (this vol. ii, 132). The authors maintain that the criticisms of König (this vol. ii, 210) are invalidated by the publication of these details, and do not need further reply.

T. S. P.

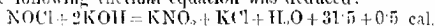
**Formation and Properties of Nitrosyl Chloride.** FRIE BRINER and (Mlle.) Z. PYLKOV (*J. Chim. phys.*, 1912, 10, 610–679. Compare Bonbrav and Guye, A., 1911, ii, 599).—The known methods of preparing nitrosyl chloride are due to Gay Lussac, Tilden, and Muller respectively. Gay Lussac's method of synthesis by admixture of nitric oxide and chlorine leads to a product containing chlorine in solution. The animal charcoal sometimes employed as a catalytic agent is not really necessary, and does not affect the yield. Muller's method of preparation by passing gaseous hydrogen chloride into liquid nitrogen dioxide at  $-10^\circ$  also leads to a product which is contaminated with chlorine and oxides of nitrogen. The authors find that when hydrogen chloride is passed into liquid nitrogen trioxide, nitrosyl chloride is produced according to the equation  $\text{N}_2\text{O}_3 + 2\text{HCl} \rightarrow 2\text{NOCl} + \text{H}_2\text{O}$ , but the interaction of nitrosyl sulphate (chamber crystals) and potassium chloride (Tilden) gives the least contaminated product.

The nitrosyl chloride was purified by crystallisation and fractional distillations in presence of phosphoric oxide. The densities, viscosities, surface tensions, vapour tensions, and critical temperature were measured over a range of temperatures from  $-65^\circ$  to  $+40^\circ$ , and from these the latent heat of vaporisation and the critical pressure were obtained by calculation.

Since the atomic volumes of nitrogen and chlorine are somewhat uncertain, the molecular weight of nitrosyl chloride cannot be estimated from the density measurements alone, but the values obtained for the other properties are available for this purpose. Ramsay and Shields' method and the ratio of the boiling point to

the density (Louginescu) lead to the conclusion that nitrosyl chloride is slightly polymerised. From the boiling point and surface tension values (Kistiakowski's formula), b. p., surface tension, and vapour tension (Dutoit and Mojeau), b. p., surface tension, and critical temperature (Walden), surface tension and latent heat (Walden), and the viscosity-temperature curve (Batschinski), the conclusion is drawn that nitrosyl chloride is not polymerised. It is urged that Ramsay and Shields' method gives no certain information as to polymerisation in the bulk of the liquid away from the surface film.

The heat developed on passing nitrosyl chloride into excess of potassium hydroxide in a Dewar calorimeter was compared with the heat of neutralisation of sulphuric acid under like conditions, and the following thermal equation was deduced:



The following equations are exothermic, and the thermal values give some idea of the relative facility with which nitrosyl chloride is prepared by different methods:  $\frac{1}{2}\text{N}_2\text{O}_3 + \text{HCl} = \text{NOCl} + \frac{1}{2}\text{H}_2\text{O} + 8.3 \text{ cal.}$ ;  $\text{NO} + \frac{1}{2}\text{Cl}_2 = \text{NOCl} + 14.4 \text{ cal.}$ ;  $\frac{1}{2}\text{N}_2\text{O}_4 + 2\text{HCl} = \text{NOCl} + \text{H}_2\text{O} + \frac{1}{2}\text{Cl}_2 + 18.5 \text{ cal.}$  The following equations being endothermic, the reactions do not occur at ordinary temperatures:  $\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 + \frac{1}{2}\text{Cl}_2 = \text{NOCl} - 7.2 \text{ cal.}$ ;  $\frac{1}{2}\text{N}_2\text{O}_4 + \frac{1}{2}\text{Cl}_2 = \text{NOCl} + \frac{1}{2}\text{O}_2 - 4.6 \text{ cal.}$

The heat of dissociation into nitric oxide and chlorine being negative ( $-14.4 \text{ cal.}$ ), dissociation should increase with rising temperature. The heat of dissociation calculated from Sudborough and Millar's vapour-density measurements (T., 1891, **59**, 74, 271) by van't Hoff's formula varies somewhat, but in all cases considerably exceeds  $-14.4 \text{ cal.}$ , a result which is attributed to a disturbance of the equilibrium by the partial dissociation of nitric oxide at the temperatures employed. R. J. C.

**Borates. The System  $\text{B}_2\text{O}_3-(\text{NH}_4)_2\text{O}-\text{H}_2\text{O}$  at  $30^\circ$ .** II. UMBERTO SPORCI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 90—95. Compare this vol. ii, 213).—The paper contains the numerical results of this investigation, of which the conclusions have already been described. R. V. S.

**The System  $\text{SiO}_2$ .** ANDREAS SMITS and KURD ENDELL (*Zeitsch. anorg. Chem.*, 1913, **80**, 176—184. Compare Endell and Riecke, this vol. ii, 134).—The relations of tridymite to cristobalite and quartz are still very uncertain. The attempt is now made to apply Smits' dynamic theory of allotropy to the case of silica.

It is sufficient to assume only two different kinds of molecules, which together form solid solutions. Three discontinuities in the solid solutions are assumed.  $\beta$ -Cristobalite is stable between  $165^\circ$  and  $800^\circ$ , and is then converted by slow cooling in presence of mineralisers into  $\beta$ -quartz, which in turn always changes into  $\alpha$ -quartz at  $575^\circ$ . Under ordinary conditions of cooling, however  $\beta$ -cristobalite persists below  $800^\circ$ , and passes at  $230^\circ$  into acristobalite. In similar manner, the metastable tridymite has a transformation point at  $130^\circ$ , but in order to account fully for tridymite it may be necessary to assume a pseudo-ternary system.

A pressure-temperature diagram has also been constructed, which takes account of  $\alpha$ - and  $\beta$ -quartz,  $\alpha$ - and  $\beta$ -cristobalite, and silica glass. In all cases increase of pressure raises the melting and transformation points.

C. H. D.

**The Crystallising Power of Silicates.** ERWIN KITTL (*Zeitsch. anorg. Chem.*, 1913, 80, 79—92. Compare this vol., ii. 47; Schumov-Dobano and Dittler, A., 1912, ii. 170).—The possible forms of the relation between velocity of crystallisation and viscosity are discussed. Complete crystallisation usually occurs when the maximum velocity falls in the region of low viscosity, whilst in the opposite case the silicate forms a glass. The number of crystallisation centres per sq. cm. is given for a series of silicates, and varies, under the conditions of the author's experiments, between 1.3 for calcium magnesium metasilicate and 220,000 for magnesium orthosilicate or 450,000 for a mixture,  $5\text{Mg}_2\text{SiO}_4 + \text{Fe}_2\text{SiO}_4$ . Manganese orthosilicate has a much smaller number of centres than other orthosilicates, and, unlike them, forms radiating groups of crystals.

C. H. D.

**Equilibria in Binary Systems of Fluorides.** NIKOLAI A. PRISNIN and A. V. BASKOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 82—101).—Investigation of the melting-point curves of mixtures of fluorides leads to the following results.

With the fluorides of all the alkali metals, aluminium fluoride forms definite compounds of the cryolite type,  $\text{AlF}_3 \cdot 3\text{MF}$ . Further, in the cases of sodium, potassium, and rubidium fluorides, there probably exist other compounds with compositions analogous to that of chiolite,  $2\text{AlF}_3 \cdot 3\text{MF}$ . Cryolite,  $\text{AlF}_3 \cdot 3\text{NaF}$ , and the similar compounds,  $\text{AlF}_3 \cdot 3\text{KF}$  and  $\text{AlF}_3 \cdot 3\text{RbF}$ , form polymorphous modifications, stable below  $600^\circ$ , below  $300^\circ$ , and below  $350^\circ$  respectively.

Some of the fused mixtures of aluminium fluoride with potassium and rubidium fluorides are red, and some of those with caesium fluoride are red and others green.

The systems  $\text{NaF} + \text{PbF}_2$ ,  $\text{NaF} + \text{CdF}_2$ , and  $\text{KF} + \text{BaF}_2$  form eutectic mixtures containing 67.5 mol. %  $\text{PbF}_2$ , 47.5 mol. %  $\text{CdF}_2$ , and 56%  $\text{BaF}_2$  respectively, the corresponding melting points being  $540^\circ$ ,  $660^\circ$ , and  $750^\circ$ . Cadmium fluoride melts at  $1110^\circ$ .

With  $\text{KF} + \text{CeF}_3$  the eutectic point lies at  $660^\circ$ , and corresponds with 21 mol. %  $\text{CeF}_3$ , whilst with  $\text{NaF} + \text{FeF}_2$  the eutectic temperature is  $892^\circ$  and the content of ferric fluoride, 35 mol. %. Zinc and sodium fluorides form a eutectic mixture, melting at  $682^\circ$ .

The molecular lowering of the crystallising temperature of sodium fluoride (100 grams) by lead, cadmium, and aluminium fluorides amounts to 187, 189.5, and 221 respectively.

In none of the systems examined was the formation of solid solutions observed.

T. H. P.

**Double and Complex Salts. I.** NILRATAN DHAR (*Zeitsch. anorg. Chem.*, 1913, 80, 43—58).—The methods of distinguishing between double and complex salts are reviewed, and determina-

tions of conductivity of a number of salts are given, with the object of filling gaps in the investigations of Werner and others.

Potassium cobaltinitrite,  $K_3Co(NO_2)_6$ , and the sodium salt are complex salts with four ions. Potassium bismuth thiosulphate,  $K_3Bi(S_2O_3)_3 \cdot 11H_2O$ , is a complex salt yielding four ions, one of which,  $Bi(S_2O_3)_3$ , is tervalent. It does not give the reactions for bismuth. Barium chromioxalate and potassium ferrioxalate are complex, whilst potassium antimonyl oxalate is a double salt. Potassium cobalticyanide and cobaltous mercurithiocyanate contain stable complexes, whilst potassium cobaltothiocyanate is a typical double salt. Other complex salts are potassium chromithiocyanate, sodium nitroprusside, and a number of cobaltamine salts, the latter undergoing partial resolution in dilute solution. C. H. D.

**The Transformation Undergone by Heated Calcium Carbide.** EMIL BRINER and A. KUHN (Compt. rend., 1913, 156, 620-622).—Contrary to the results of Erlwein, Warth, and Bentner (A., 1911, ii, 396), the authors find that, on heating calcium carbide to 900° in unglazed porcelain tubes it is partly decomposed into its elements, and does not form a lower carbide. The residue does not give off hydrogen on treatment with water, but the absence of calcium thus proved is probably due to volatilisation or combination with the substances of which the tube is made. W. G.

**Supposed Occurrence of a Peroxide in Calcium Hydroxide, which has been Exposed to Air, and in Aragonite.** HUGO FUZ (J. pr. Chem., 1913, [ii], 87, 208-227).—On exposure to air, calcium hydroxide gives, with hydrochloric acid and starch-potassium iodide solution, a blue coloration, the intensity of which increases with the time of exposure. This coloration is considered by Vaubel (A., 1912, ii, 1172) to be due to formation of a hydroperoxide.

The author finds, however, that even after long exposure no hydrogen peroxide could be detected either by the chromic acid or titanous acid reactions, on treating the hydroxide with hydrochloric acid, although the starch-iodide reaction was quite pronounced. The exposed calcium hydroxide gives a pink coloration with an acetic acid solution of sulphanilic acid and  $\alpha$ -naphthylamine, indicating the presence of a nitrite, and it is therefore probable that the starch-iodide reaction is due to the formation of a nitrite by the absorption of nitrous oxides from the air. Vaubel has also shown (A., 1912, ii, 89) that aragonite rapidly develops a blue coloration on treatment with hydrochloric acid and starch-iodide, whilst in the case of calcite the coloration develops more slowly and is much less intense. This difference he referred to the presence of a small amount of peroxide in the aragonite.

The author shows, however, that the coloration is due to the presence of iron, the slower development in the case of calcite being due to its smaller iron content. F. B.

**Preparation of a Complex Salt of the Apatite Type and its Bearing on the Formation of Bone.** THEODOR GASSMANN (Z. physiol. Chem., 1913, 83, 403-406).—On heating phosphotri-calcium

carbonate,  $\left[ \text{Ca} \begin{pmatrix} \text{OPO}_3\text{Ca} \\ >\text{Ca} \\ \text{OPO}_3\text{Ca} \end{pmatrix} \right]_3 \text{CO}_3$ , derived from ashed teeth or bones, with somewhat more than the corresponding molecular quantity of calcium chloride for fifteen minutes at a red heat, and extracting the mass with acetic acid, a colourless amorphous residue of *phosphocalcium chloride*,  $\left[ \text{Ca} \begin{pmatrix} \text{OPO}_3\text{Ca} \\ >\text{Ca} \\ \text{OPO}_3\text{Ca} \end{pmatrix} \right]_3 \text{Cl}_2$ , is obtained.

The calcium chloride is not extracted from this by means of water; this disproves the composition,  $9\text{Ca}_3\text{PO}_4\text{CaCl}_2$ . The conversion of the carbonate into the chloride is considered to establish the presence of the apatite complex in bones. E. F. A.

**Dispersion of the Birefringence of Mixed Crystals of Strontium and Lead Dithionates.** H. AMBRONX (*Zeitsch. Krist. Min.*, 1913, 52, 48—57).—The anomalous dispersion exhibited by these crystals is discussed. L. J. S.

**The Hydrate and Ammoniate of Glucinum Chloride.** K. MUELETNER and H. STEINMETZ (*Zeitsch. anorg. Chem.*, 1913, 80, 71—78).—When ether is added to an aqueous solution of glucinum chloride, and the mixture is cooled in ice and saturated with hydrogen chloride, a crystalline precipitate is formed, which, after drying in a vacuum over sulphuric acid, has the composition  $\text{GlCl}_2 \cdot 4\text{H}_2\text{O}$ . It does not contain combined ether, as supposed by Parsons (*ibid.*, 1904, 40, 408), and alcohol may be used in place of ether. The anhydrous chloride cannot be obtained by heating in dry hydrogen chloride or chlorine; the water is firmly held.

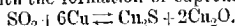
The anhydrous chloride is prepared by heating a mixture of pure glucinum chloride and carbon in dry chlorine. The carbon is sugar charcoal, purified by boiling with hydrochloric acid and heating to redness in chlorine. The sublimed chloride combines readily with dry ammonia, forming the *tetra-ammoniate*,  $\text{GlCl}_2 \cdot 4\text{NH}_3$  (compare Ephraïm, A., 1912, ii, 546). If the mixture is allowed to become hot, the composition approaches more nearly to  $\text{GlCl}_2 \cdot 2\text{NH}_3$ .

C. H. D.

**The Solubility of Sulphur Dioxide in Molten Copper Alloys.** ADOLF STEVERTS and E. BERGMAN (*Zeitsch. physikal. Chem.*, 1913, 82, 257—270. Compare A., 1910, ii, 410, 851).—The solubility of sulphur dioxide is determined in gold, silver, and platinum alloys of copper, and in copper containing known amounts of cuprous oxide or cuprous sulphide by the same method as previously described (*loc. cit.*). In the case of the metal alloys, particularly of those with gold, it is shown that solubility decreases with increasing gold concentration. This decrease in solubility is much more marked in the case of the oxide and sulphide mixtures, the oxide decreasing the solubility about three times as much as the sulphide. The amount of decrease in the solubility is approximately proportional to the concentration of these substances for dilute solutions, that is,



up to about 7%, but above this figure the proportionality ceases. The relationship between solubility, temperature, and pressure is the same as in the case of pure copper. The solubility increases with increasing temperature, and the quantity dissolved varies with the square root of the pressure, that is,  $p^2/m$  is constant for concentrations up to about 7%. The experimental results can be partly explained by the assumption that the sulphur dioxide is decomposed in solution with the formation of cuprous sulphide and oxide,



From this an equilibrium constant ought to be obtained from the expression:

$$(\text{Cu}_2\text{O})^2 \cdot (\text{Cu}_2\text{S}) / (\text{Cu})^6 \cdot (\text{SO}_2) = K_1,$$

and since in dilute solutions the concentration of the copper can be regarded as constant, and the pressure of the sulphur dioxide can be kept constant:

$$(\text{Cu}_2\text{O})^2 \cdot (\text{Cu}_2\text{S}) = K_2.$$

This latter expression is only found to hold between the concentrations 0.85—1.7 molecules  $\text{Cu}_2\text{S}$  and 1.7—1.2 mols.  $\text{Cu}_2\text{O}$ . Consequently the expression can only be said to hold in a qualitative manner. The authors are of the opinion that a considerable loss of sulphur dioxide, and consequently of cuprous oxide, occurs through the formation of a slag due to interaction of cuprous oxide with the porcelain tube.

J. F. S.

**Volatilisation of Certain Binary Alloys in High Vacua**  
 ARTHUR J. BERRY (*Proc. Camb. Phil. Soc.*, 1913, **17**, 31—33. Compare A., 1912, ii, 161).—The behaviour of certain alloys when subjected to distillation in a high vacuum has been investigated. An alloy of copper and cadmium was found to have been completely separated into its constituents when distilled at about 600°. In the case of a cadmium-magnesium alloy containing excess of cadmium, both metals distilled over, and it seems probable that the composition of the distillate is dependent on the temperature of volatilisation. On distillation of alloys of lead and magnesium, containing the two metals in approximately equivalent proportions, at about 680°, it was found that the distillate consists almost entirely of magnesium, traces only of lead being present. Microscopic examination of the distillate showed the presence of small quantities of steel-blue crystals embedded in a matrix of magnesium. In the neighbourhood of these crystals, the distillate underwent rapid corrosion on exposure to the air, with the formation of a black powder. This seems to show that the crystals are those of the compound  $\text{Mg}_2\text{Pb}$ .

H. M. H.

**The Reduction of Solutions of Copper Sulphate by Sodium Hypophosphite and Sodium Hyposulphite.** JAMES E. MYERS and JAMES B. FIRCH (*Zeitsch. anorg. Chem.*, 1913, **80**, 93—103. Compare P., 1912, **28**, 101).—An apparatus is described, in which the reacting liquids may be mixed and filtered in an atmosphere of carbon dioxide. Copper sulphate and sodium hypophosphite yield at 70° cuprous hydride,  $\text{Cu}_2\text{H}_2$ , which is reddish-brown and decom-

passes suddenly at  $60^{\circ}$  when dry. The longer the reaction lasts, the lower is the proportion of hydrogen in the product. At the ordinary temperature the product, after a few hours, contains cuprous oxide, hydride and phosphate, and is explosive. Cupric hydride is not an intermediate product.

Copper sulphate and sodium hyposulphite yield copper or copper sulphide. C. H. D.

**The Purification and Atomic Weight of Yttrium.** RICHARD J. MEYER and J. WEORIXEN (*Zeitsch. anorg. Chem.*, 1913, 80, 7--35).

The following methods are suitable for the fractionation of mixtures containing yttrium. The precipitation of dichromate solutions with potassium chromate separates yttrium well from terbium and gadolinium, but is most applicable to mixtures from which most of the terbium group has been removed by other methods, when it yields pure yttria.

Fractional crystallisation of the ethyl sulphates is tedious, but is suitable for large quantities. Precipitation with potassium ferrocyanide yields nearly pure yttria, but the yield is small, and the precipitates are not readily filtered. Crystallisation of the double ammonium tartrates is unsuccessful, as is also the fractional hydrolysis of these salts by water, ammonia, or magnesia.

A new method is described, depending on the hydrolysis of solutions of the phthalates by heat. This method rapidly removes the erbium group, and gives a large yield of a product consisting mainly of yttria, which is then conveniently purified by fractionally precipitating a slightly acid solution of the nitrates with potassium iodate.

The atomic weight of yttrium is found by the sulphate method to be 88.6, the international value, 89.6, being too high. The material used is purified by the iodate method, and allowance is made for the stability of traces of acid sulphate at  $500^{\circ}$ . Former determinations are critically reviewed.

The purified material gives only the strongest line or lines of erbium, ytterbium, gadolinium, terbium, dysprosium, and holmium in the arc spectrum. The phosphorescence in a cathode light vacuum is a bright yellow.

Yttria is diamagnetic, the values found by EDGAR WEDEKIND,  $\chi, 10^6$ , being for  $\text{Se}_2\text{O}_3 = 0.05$ ;  $\text{Y}_2\text{O}_3 = 0.11$ ;  $\text{La}_2\text{O}_3 = 0.18$ .

Pure yttria has  $D_D$  4.81.

C. H. D.

**The Rare Earths of the Carolina Monazite Sands.** CHARLES JAMES (*Chem. News*, 1913, 107, 110-111; *J. Amer. Chem. Soc.*, 1913, 25, 235-239). The bromate method has been applied to the fractionation of the rare earths derived from the monazite sands of Carolina, and it is shown that these sands contain, in addition to lanthanum, cerium, praseodymium, and neodymium, considerable quantities of samarium, gadolinium, and yttrium; small amounts of dysprosium, holmium, and erbium; and minute amounts of europium, terbium, thulium, and ytterbium, etc. Erbium occurs in much smaller quantities than holmium and dysprosium, and this

fact probably accounts for the anomalous behaviour of certain fractions which has been observed by other workers.

The oxalates obtained from the more soluble double sulphates are recommended as a source of samarium, gadolinium, europium, terbium, dysprosium, and holmium. T. S. P.

**The Electro-Metallurgy of Aluminium.** P. P. FRODOV and V. L. LEVINSKY (*Zetsch. angew. Chem.*, 1913, 80, 115—154).—The process of manufacture of aluminium by the electrolysis of solutions of alumina in fused cryolite has been investigated by physico-chemical methods. This has involved the study of the system  $\text{AlF}_3\text{--NaF}$ , and of the influence of other compounds on the equilibrium.

Pure aluminium fluoride cannot be obtained by heating the hydrated salt, as hydrolysis takes place, but the impure product may be sublimed at  $1100^\circ$ , yielding large crystals of the pure fluoride when the cooling is not too rapid. The anhydrous salt is not attacked, even by concentrated sulphuric acid.

The freezing-point curve shows that cryolite,  $3\text{NaF}\cdot\text{AlF}_3$ , is a very stable compound, m. p.  $1000^\circ$ . A second compound is also formed,  $5\text{NaF}\cdot\text{AlF}_3$ , identical with the mineral chiolite. This does not melt, but is transformed at  $725^\circ$  into cryolite and liquid. There are eutectic points at  $880^\circ$  and  $685^\circ$  and at 14 and 46.4 mol.  $\text{AlF}_3$  respectively. Solid solutions are only formed from 0 to 1 mol.  $\text{AlF}_3$ . The transformation of monoclinic into regular cryolite takes place at  $565^\circ$ , and is accompanied by a change of volume. From 50 mol.  $\text{AlF}_3$  onwards the mixtures volatilise.

Cryolite and alumina form solid solutions, the freezing-point curve up to 21%  $\text{Al}_2\text{O}_3$  being continuous, with a minimum at 15 and  $935^\circ$ . The solubility of alumina in the eutectic  $\text{NaF}\cdot\text{Na}_3\text{AlF}_6$  is greater than in cryolite, and the curve also passes through a minimum. In this case cryolite and aluminate are probably formed.  $6\text{NaF} + \text{Al}_2\text{O}_3 = \text{Na}_3\text{AlF}_6 + \text{Na}_3\text{AlO}_4$ , the excess of cryolite acting as a solvent, as alumina is insoluble in fused sodium fluoride. The addition of aluminium fluoride to cryolite diminishes its solvent power for alumina.

A difference of potential of 2.1—2.2 volts is required for the continuous production of aluminium. The electrolysis observed with 1.3 volts is due to the formation of aluminium carbide,  $\text{Al}_4\text{C}$ . The anode effect sometimes observed is due in part to an accumulation of alumina in the neighbourhood of the anode.

The loss of aluminium by emulsification of the metal in the bath and by the formation of carbide has also been determined in certain cases. The yield does not exceed 70%, owing to emulsification of aluminium. It is necessary to stir the electrolyte, to add alumina, and to break up the crust from time to time. The use of a porous anode may be of advantage.

A bath of low melting point is best obtained by using a double mixture in place of cryolite, and keeping the concentration of the alumina near 7.5%. This mixture has a lower density than cryolite. Calcium fluoride lowers the melting point, but diminishes the

solubility of alumina and increases the density. Calcium and aluminium fluorides form a eutectic at  $815-820^{\circ}$ , containing 37.5 mol. %  $\text{AlF}_3$ . Some points in the ternary system have been determined. C. H. D.

**Action of Distilled Water on Pure Aluminium.** II. ALBERTO SCALA (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 95-102. Compare this vol., ii, 220).—The corrosion of impure aluminium by distilled water, previously described, is due to the traces of iron contained in the metal. The aluminium used, although much purer than ordinary commercial aluminium, had the following composition:

Al.	Fe.	Si.	Cu.	Na.	Total.
99.371	0.079	0.464	traces	0.068	99.981

If a piece of iron is immersed in water contained in an aluminium vessel, blackening and corrosion commences much sooner than in a similar vessel containing distilled water only. The presence of the actual metal is not necessary, for distilled water in which iron has previously been immersed is also very active in causing the corrosion. A solution of colloidal ferric oxide has no action on the aluminium. The solvent action of water is very rapid and pronounced when, instead of the impure aluminium, an alloy of iron and aluminium (about 15% of iron) is used. The author suggests a mechanism for the reaction, in which a colloidal ferrous oxide probably plays a part. R. V. S.

**The Carbides of Manganese and Nickel.** OTTO RUFF and ERNOLD GERSTEN (*Ber.*, 1913, 46, 409-413).—Trimanganocarbide,  $\text{Mn}_3\text{C}$  (compare Stadelé, A., 1903, ii, 392), was prepared from manganese and carbon by heating a mixture of these two substances at  $1600^{\circ}$  for twenty minutes in a vacuum electric furnace under a pressure of 20 mm. The manganese was prepared by the thermit method, and had the following composition: Mn, 98.68%, Fe, 0.42%, Al, 0.55%, C, 0.02%, insoluble residue, 0.25%; melting-point determinations gave the values,  $1242^{\circ}$ ,  $1247^{\circ}$ , and  $1239^{\circ}$ . The regulus obtained contained nests of crystals in the centre, which could be easily separated from the main mass; the crystals consisted of glistening fibres and needles, and after separating the admixed carbon by means of acetylene tetrabromide, were found to have a composition corresponding with the formula  $\text{Mn}_3\text{C}$ . The main mass of the regulus was then finely powdered, the graphite and carbon removed with acetylene tetrabromide, and the residue found also to consist of the pure carbide. The hardness of trimanganocarbide lies between that of talc and gypsum; the molecular volume is 25.70, as compared with the calculated value 29.80. The following thermochemical data were obtained, the products of combustion being analysed in each case, in order to make any necessary corrections. Molecular heat of formation of  $\text{Mn}_3\text{O}_4$ ,  $329.0 \pm 0.74$  Cal. (Le Chatelier's value is 327.33 Cal.); the manganese burns completely to  $\text{Mn}_3\text{O}_4$ . Molecular heat of combustion of trimanganocarbide,  $110.9 \pm 2.0$  Cal., the product of combustion being  $\text{Mn}_3\text{O}_4$ .

The molecular heat of formation of trimanganocarbide from manganese and graphite is then calculated to be  $12.9 \pm 2.14$  Cal. (Le Chatelier's value is 9.34 Cal.).

The solubility of carbon in nickel reaches a maximum at 2100°, and the composition of the fusion corresponds with the formula  $\text{Ni}_3\text{C}$ , that is, with trinickelcarbide (compare Ruff and Martin, A., 1912, ii, 354). The carbide undergoes considerable decomposition on cooling, however, even when the fusion is quenched; also the resulting mass is so tough that it is impossible to powder finely the quenched mass, and then resort to levigation for obtaining the pure carbide. The following thermochemical data therefore hold for an impure material as far as the carbide is concerned, containing only 4.39% of carbide, but the substances used and the products formed were always analysed in order to make necessary corrections. Molecular heat of formation: of nickel oxide ( $\text{NiO}$ ),  $51.5 \pm 0.7$  Cal., of trinickelcarbide,  $-394 \pm (\text{ca.}) 10$  Cal.

Comparison of the molecular heats of formation of the carbides of iron (see this vol., ii, 296), manganese, and nickel accounts for the great instability of nickel carbide, corresponding with the fact that nickel is the noblest element. The molecular volumes of the carbides of iron and manganese indicate that the contraction occurring when formed from their elements is of the same order. Both the carbides of iron and manganese are soft, so that the hardness of alloys containing these substances cannot be due to them existing as such, but probably depends on the hardness of their solid solutions (compare Kurnakov and Shentschinsky, A., 1908, ii, 932). T. S. P.

**Some Properties of an Industrial Electrolytic Iron.** L. G. GUILLET and A. PORTEVIN (*Compt. rend.*, 1913, 156, 702—705. Compare Broniewski, this vol., ii, 288).—A physical study of electrolytic iron prepared on an industrial scale. The metal, supersaturated with hydrogen, is very fragile, its hardness being considerably diminished by annealing, when its micrographic structure becomes normal. The presence of the hydrogen does not influence the transition temperatures. The electrical resistance of a centimetre cube, corrected for the presence of sulphur and arsenic, is 11.92 micro-ohms before annealing, and 9.98 micro-ohms after. W. G.

**The Corrosion and Rusting of Iron which has been Treated by the Sherard Process.** FRANZ HALLA (*Zeitsch. Elektrochem.*, 1913, 19, 221—226).—The Sherard process consists in galvanising iron by surrounding it with zinc dust and then heating in a furnace for about two hours at a temperature somewhat below the melting point of zinc. Wrought iron nails were treated by this process and their corrosion studied by immersing them in 3.2% sulphuric acid for definite periods. The velocity of solution of the zinc coating was thus determined. It is shown that in all cases the velocity passes through a minimum, then reaches a constant stage, which is maintained until nearly the whole of the coating is dissolved, and then is slightly increased to the end of the process. Theoretical explanations are given for the changes in the velocity of solution.

Experiments on the rusting of specimens are also described. A quantity of treated nails are placed, some in water, and some above it. It is shown that even in one day rusting has taken place, as evidenced by the appearance of a white, flocculent precipitate of zinc hydroxide, which after a while is tinted brown. Iron treated by this process is shown to be more resistant to rusting and corrosion than that treated by the other processes, that is, galvanic deposition or immersion in molten zinc.

J. F. S.

**The Reactions between Ferrous Oxide and Carbon and between Carbon Monoxide and Iron.** VICTOR FALCKE (*Ber.*, 1913, **46**, 743—750).—The object of the present investigation was to determine whether the equilibrium in the system with the solid phases FeO, Fe, and C, and the gas phase CO, CO<sub>2</sub>, varies with the kind of amorphous carbon used (compare Baur and Glasner, A., 1903, ii, 423; Schenck and others, A., 1905, ii, 519; 1907, ii, 470). The apparatus used was similar to that of Schenck and Heller (A., 1905, ii, 519), and at first the ferrous oxide used was prepared by heating ferrous oxalate at 300° (compare Schenck and Heller, *loc. cit.*). It was found, however, that this was not satisfactory, since even at 700° gas is still evolved; consequently the results of Schenck and Heller are not trustworthy.

It was further found that the pressure set up when a mixture of 2 grams of ferrous oxide with 1.5 grams of iron (Kahlbaum) is heated at 530—660° is independent of the presence of sugar carbon; the ferrous oxide contained 0.5% of carbon, and before being used was heated in a vacuum for a long time at 650°.

Further experiments showed that the reaction between iron and carbon monoxide at 650° varies, according to whether the gas is led in a continuous current over the iron, or allowed to remain in contact with it in a closed vessel. In the former case, much carbon is deposited, whereas in the latter case, if, after equilibrium has been obtained, the iron is dissolved in hydrochloric acid, all the carbon is evolved as carbon dioxide, and none left behind as an insoluble residue. The way in which the carbon monoxide reacts in the latter case is uncertain.

The above results show that the reaction between iron and carbon monoxide is more complex than is generally assumed, and also that the conclusions and theories of Schenck and his co-workers (*loc. cit.*) are invalid, because based on inaccurate experimental evidence. The object of the author's investigation was thus not attained.

T. S. P.

**Action of Sulphurous Acid on the Sulphides of Iron, Zinc, and Manganese.** WILLIAM E. HENDERSON and HARRY D. WEISER (*J. Amer. Chem. Soc.*, 1913, **35**, 239—244). It is well known that the freshly precipitated sulphides of iron, zinc, and manganese are readily soluble in sulphurous acid, whilst those of nickel and cobalt are only sparingly so. As conflicting statements have been made with regard to the nature of the reaction and the products formed, the present investigation was undertaken.

When freshly precipitated iron, zinc, or manganese sulphide is suspended in water and a current of sulphur dioxide introduced, the sulphide rapidly dissolves, and the sulphite of the metal is gradually deposited, the reaction being represented by the equation:  $MS + H_2SO_3 = MSO_3 + H_2S$ . On continuing to pass sulphur dioxide into the mixture, the sulphite dissolves to form the hydrogen sulphite. If the solution of the hydrogen sulphite is boiled, the sulphite is re-deposited. The solution now contains thiosulphate, which is produced by the action of sulphur, formed by the interaction of sulphurous acid and hydrogen sulphide, on the hydrogen sulphite, thus:  $M(HSO_3)_2 + S = MS_2O_3 + H_2O + SO_2$ . These and other experiments show that the reaction between sulphurous acid and the sulphides of zinc, iron, and manganese is a double decomposition of the usual type, and that, in so far as the conditions lead to the oxidation of the liberated hydrogen sulphide by the sulphurous acid, a certain amount of thiosulphate is produced by a secondary reaction.

E. G.

**Alloys of Cobalt with Chromium and Other Metals.** ELWOOD HAYNES (*J. Ind. Eng. Chem.*, 1913, 5, 189—191).—Tungsten alloys readily with chromium and cobalt in all proportions. Taking an alloy of chromium and cobalt as the basis, and keeping the proportion of chromium at 15% of the entire mixture, the alloy gradually increases in hardness with increasing percentage of tungsten. When the quantity of tungsten rises to 5%, the alloy becomes distinctly harder; 10% tungsten gives an alloy suitable for both cold chisels and wood-working tools; 15%, an alloy excellent for cold chisels; a 20% alloy makes good lathe tools for cutting steel and other metals at moderate speeds, etc. A 40% alloy is so hard that it readily scratches not only glass, but quartz, and can be used for turning cast iron.

Very similar results are obtained when the tungsten is replaced by molybdenum. The 25% alloy has a magnificent colour and lustre. If carbon, boron, or silicon be added to any of the alloys, it renders them much harder, but they also become more brittle.

When the percentage of chromium is kept at 25% instead of 15, the addition of either tungsten or molybdenum still increases the hardness of the alloy.

T. S. P.

**The Violet Chromium Sulphates.** A. SÉNÉCHAL (*Compt. rend.*, 1913, 156, 552—555).—Two violet chromium sulphates are at present known, namely, the hydrates having respectively  $15H_2O$  and  $17H_2O$  (compare Weinland and Krebs, A., 1906, ii, 453). A study of the vapour tension, rate of dehydration, and heat of solution of these hydrates now leads to the conclusion that there are five possible violet chromium sulphates, being the hydrates containing respectively 12, 14, 15, 16, and 17  $H_2O$ .

W. G.

**The Reduction of Tungstic Acid and the Lower Oxidation Stages of Tungsten.** I. OSCAR OLSSON (*Ber.*, 1913, 46, 566—582).

—All the reduction experiments were carried out with a solution of tungstic acid in concentrated hydrochloric acid, which was made

by adding gradually a solution of potassium tungstate to boiling hydrochloric acid. Success in obtaining such a solution is obtained only when the conditions given by the author are strictly observed. Double salts of tervalent tungsten can then be obtained from this solution as follows: The solution is reduced with tin at 40–60° until the colour is a deep green; it is then rapidly filtered through glass wool, and the filtrate saturated with hydrogen chloride, cooling meanwhile with a freezing mixture. A yellowish-green to yellowish-brown powder gradually separates; the current of hydrogen chloride is stopped after six to seven hours, and the crystals allowed to deposit for twenty-four hours, after which time they are collected, washed with alcohol and ether, dried in a current of carbon dioxide, and preserved in a carbon dioxide desiccator. The *potassium* salt thus obtained has the composition  $K_2W_3Cl_8$ , and by double decomposition in hydrochloric acid solutions of rubidium chloride, caesium sulphate, and thallous chloride respectively, the *rubidium*, *caesium*, and *thallium* salts were prepared. The *ammonium* salt was prepared similarly to the potassium salt, using a solution of ammonium metatungstate as the starting point. All these salts are anhydrous, have the general formula  $M_2W_3Cl_8$ , and crystallise in thin, hexagonal plates, which have a greenish-yellow colour in transmitted light. The concentrated aqueous solutions are green, becoming greenish-yellow on dilution. The solubility decreases as the atomic weight of the alkali metal increases. They can be preserved for several days when dry, but are rapidly oxidised when moist. The solutions show no characteristic absorption bands, but a general absorption at either end of the spectrum, the visible spectrum extending from  $\lambda=700$  to  $\lambda=520$  for a solution of 1 gram of the potassium salt in 100 c.c. of 3% hydrochloric acid, the thickness of the absorbing layer being 1 cm. For a solution containing 0.1 gram of the salt per 100 c.c., the spectrum extends from  $\lambda=700$  to  $\lambda=490$ .

When the solution of tungstic acid aforementioned is reduced with tin at the ordinary temperature, it first becomes light blue in colour, the colour then gradually deepens, and finally suddenly changes to an intense reddish-violet colour, similar to that of permanganate. This colour persists for a long time, and a small quantity of a dark green powder deposits, consisting of quadric, tabular crystals, which are red in transmitted light. These appear to be a *potassium double salt* of quadrivalent tungsten, having the empirical formula  $K_2W(OH)Cl_4$ . The salt is stable when dry, but oxidises rapidly when moist. The absorption spectrum of the hydrochloric acid solution is similar to that of the tervalent compounds, the visible spectrum for a solution of 1 gram in 150 c.c. of 4% hydrochloric acid and a thickness of 1 cm. extending from  $\lambda=730$  to  $\lambda=610$ .

T. S. P.

**The Preparation of Metallic Vanadium** OTTO RUFF and WALTER MARTIN (*Zeitsch. anorg. Chem.*, 1913, 80 59, 64. Compare A. E. 166; Prandl and Manz, this vol. ii. 142).—The authors' data refer to metal obtained free from slag by fusing in the arc under a vanadium electrode

C. H. D.



**The System: Antimony Sulphide, Lead Sulphide.** HENRI PÉLABON (*Compt. rend.*, 1913, 156, 705–707).—A study of the melting-point curve of mixtures of the sulphides of lead and antimony. There is a eutectic at a temperature of  $482^{\circ}$ , corresponding with a mixture of 22 mols. of lead sulphide with 78 mols. of antimony sulphide. There are two transition points, one at  $568^{\circ}$ , and the other at  $610^{\circ}$ , where two compounds crystallise out corresponding in composition and appearance respectively with the minerals zinkenite,  $\text{Sb}_2\text{S}_3\cdot\text{PbS}$ , and jamesonite,  $\text{Sb}_2\text{S}_3\cdot 2\text{PbS}$ . W. G.

**Compounds of Bismuth and Iodine.** H. S. VAN KLOOSTER (*Zeitsch. anorg. Chem.*, 1913, 80, 104–112. Compare MARINO and BECARRELLI, this vol., ii, 227).—Bismuth tri-iodide readily decomposes when heated, and must be prepared by heating the compounds together in a sealed tube. It then has m. p.  $408^{\circ}$ . The equilibrium diagram of mixtures of bismuth and iodine, also determined in closed tubes, shows that the triiodide forms a sharp maximum on the freezing-point curve, and that two liquid layers are formed at  $339^{\circ}$  between 38 and 96 atomic % Bi. The eutectic point lies very close to the bismuth end. A reaction at  $281^{\circ}$  possibly represents the formation of a compound  $\text{BiI}$  from  $\text{BiI}_3$  and liquid. There is no evidence of the formation of a compound  $\text{BiI}_2$  (HERZ and GUTTMANN, A., 1908, ii, 199).

The mixtures have also been examined microscopically. The triiodide forms lamellæ, and a eutectic structure is well developed. C. H. D.

**The Sorption of Hydrogen by Palladium.** ALFRED HOLT, EDWARD C. EDGAR, and JAMES B. FIRTH (*Zeitsch. physikal. Chem.*, 1913, 82, 513–540).—From a series of experiments on the sorption (adsorption and absorption) of hydrogen, it is shown that palladium exists in an active and a passive form with respect to its action on hydrogen, and is only capable of occluding large volumes of hydrogen when in the active condition. The activity of palladium falls off rapidly after a time, but may be regained by heating. The authors come to the conclusion that the activity of the metal is due to the formation of a metastable modification. The rate at which hydrogen is occluded was studied, and it is shown that the velocity of occlusion falls off in proportion to the amount of hydrogen already present in the metal. From the experiments it is evident that hydrogen occluded by palladium is present in two forms: (1) as an adsorbed surface layer of high vapour pressure which can easily be removed by evacuating the containing vessel, and (2) as an absorbed layer which permeates the whole of the metal, but which is not of uniform concentration throughout the metal. The process of occlusion in this case is therefore shown to consist in an adsorption, which is then followed by a slow diffusion into the interior of the metal from the surface layer. The velocity of diffusion of hydrogen through palladium is studied, and shown to increase with the temperature, but it is not always the same, a fact which points to the diffusion being influenced by the condition

of the metal. The experiments show that it is unlikely that even after long periods the hydrogen has the same concentration throughout the whole of the metal.

J. F. S.

**Osmium Dioxide as a Hydrogen Carrier.** FRANZ LEHMANN (*Arch. Pharm.*, 1913, 251, 152—153. Compare Hofmann, this vol., ii, 62).—Osmium tetroxide in presence of oleic acid or liquid oils is converted into hydrated osmium dioxide, and the acid or oil is reduced to the corresponding saturated acid or glyceride; thus, a mixture of olive oil (10 grams) with 0.05 gram of osmium tetroxide, on heating and passing hydrogen during one hour, yielded a fat melting at 39°, and on further treatment gave a product melting at 45°.

T. A. H.

## Mineralogical Chemistry.

**Chalcocite Deposition.** ARTHUR COE SPENCER, (*J. Washington Acad. Sci.*, 1913, 3, 70—75).—In the presence of oxygenated waters in the upper regions of ore-deposits, sulphides (iron-pyrites and copper-pyrites) are altered, with the formation of sulphates and free acid. Solutions of ferric sulphate percolating still farther are reduced to ferrous sulphate by contact with these sulphides; and at greater depths solutions of cupric sulphate react with the unaltered primary sulphides, giving rise to secondary chalcocite ( $\text{Cu}_2\text{S}$ ). Sulphur dioxide is probably produced by these reactions, and its presence seems to favour the formation of chalcocite; further, copper-pyrites seems to have more effect in this direction than does iron-pyrites. Several equations are given to suggest the reactions which may take place under these conditions.

L. J. S.

**Immense Bloedite Crystals.** WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1913, 3, 75—76).—A deposit of nearly pure sodium sulphate (containing 1.66%  $\text{MgO}$ ) forms a crust on Soda Lake, in Cariso Plain, San Luis Obispo Co., California. In the black mud beneath this crust are found isolated crystals of bloedite, the largest of which measures  $16\frac{1}{2} \times 10\frac{1}{2} \times 3\frac{1}{2}$  cm., and weighs 652 grams. The following analysis of this material agrees with the usual formula,  $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ :

$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{SO}_3$	$\text{H}_2\text{O}$	Total
11.93	18.26	18.11	21.67	69.97

L. J. S.

**Serpentines of the Central Coast Ranges of California.** H. E. KRAMM (*Zeitsch. Kryst. Min.*, 1913, 52, 78; from *Proc. Amer. Phil. Soc.* 1910, 49, 315—349).—A petrographical description is given of the serpentine rocks of this region. The primary minerals include

olivine, enstatite, bronzite, diallage, picotite, and chromite (anal. I, from Cedar Mountain, Alameda Co.), and those of secondary origin are serpentine, chrysotile, magnetite, tremolite, hydromagnetite (anal. II), calcite, dolomite, aragonite, epsomite, limonite, and hematite.

	Al <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	Cr <sub>2</sub> O <sub>3</sub>	NiO	MnO	H <sub>2</sub> O	Total
I.	18.79	16.99	trace	8.41	55.74	trace	trace	0.09	99.82
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	CO <sub>2</sub>	H <sub>2</sub> O	Total	
II.	9.37	trace	trace	2.16	39.25	29.45	18.74	99.27	

L. J. S.

**Petrographical Investigations in the Mountains between the Septimer and Julier Passes.** HANS PETER CORNELIUS (*Jahrb. Min., 1913, Beil.-Bd., 35, 374—498*).—A detailed petrographical description of this district in Grisons, Switzerland, with several analyses of igneous and schistose rocks. The following mineral analyses are also given: I, riebeckite (or more exactly an amphibole containing 44.2% of the riebeckite molecule), isolated from a riebeckite-schist of contact-metamorphic origin; II, white diopside, forming platy masses with a porcellaneous aspect, and occurring in veins in serpentine and contact-metamorphic limestone:

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Loss on ignition	Total Spec.
I.	59.63	0.30	3.27	11.24	7.11	0.77	3.52	9.71	1.88	6.59	2.20	100.25
II.	62.52	—	—	1.16	1.10	0.11	26.68	17.59	—	—	0.93*	100.00

\*CO<sub>2</sub>.

L. J. S.

## Analytical Chemistry.

**Spectrophotometry in Analysis.** CHARLES FÉRY and EUGÈNE TASSILLY (*Ann. Patisf., 1913, 6, 73—78*).—The quantity of metal in a solution may be estimated by determining the absorption-coefficient of the solution by means of the spectrophotometer. For the estimation of iron, the thiocyanate coloration is used, and in the presence of a large excess of thiocyanate the absorption is proportional to the quantity of iron present. In the case of copper, the metal is converted into its ferrocyanide before the solution is examined.

W. P. S.

**Vegetable Indicator in Volumetric Analysis.** M. EMMANUELE POZZI-ESCOR (*Ann. Chim. anal., 1913, 18, 58—59*).—An alcoholic infusion of crushed black pansy flower is recommended as indicator in volumetric work. Mineral acids change the colour to red, but it remains bluish-violet with weak acids (acetic, formic, etc.).

Alkalis even of the weakest description change the colour to green; it is particularly sensitive to ammonia. L. DE K.

**A New Method for the Estimation of Hypochlorites.**  
HERBERT G. WILLIAMS (*Chem. News*, 1913, 107, 109).—See P., 1912, 28, 327.

**Further Observations on the New, Sensitive, and Characteristic Reactions of Bromine. III.** IDILJO GUALESCHI (*Atti R. Accad. Sci. Torino*, 1913, 48, 4—14. Compare A., 1912, ii, 989).—The author claims priority over Denigès (A., 1912, ii, 1208) for this reaction. The present paper mentions a number of other dyes which may be used instead of magenta, and also records the existence of traces of bromine in various pure salts and in the ashes of certain plants. The reaction may be used to distinguish the hydrobromides of organic bases from their other salts. The magenta reagent shows the presence of bromine in the dibromo-derivatives of the dicyanodialkylglutarimides. When a solution containing a trace of hypobromite is treated with acid, it gives the magenta reaction. The reaction may also be applied (in some cases as a convenient lecture experiment) to detect the bromine produced in such reactions as that between iodine and bromates, or the expulsion of bromine from some of its compounds by iodine. Some bromides (including those of potassium, barium, uranyl, sulphur, and lead) evolve traces of bromine when they are heated sufficiently; other bromides do so in presence of iodine, either with or without heating. Concentrated hydrobromic acid does not yield bromine, even when boiled with iodine. The decomposition of organic bromine derivatives can be recognised in the same way. Dibromoisobutane,  $\text{CMe}_2\text{Br}\cdot\text{CH}_2\text{Br}$ , tribromoethane,  $\text{CH}_2\text{Br}\cdot\text{CHBr}_2$ , and bromoisopentane,  $\text{CHMe}_2\text{CH}_2\cdot\text{CH}_2\text{Br}$ , do not yield bromine when boiled with or without iodine. Bromoform evolves bromine when heated or exposed to light, and bromal hydrate behaves similarly. R. V. S.

**An Application of the Electric Resistance Furnace to the Estimation of Oxygen in Iron and Steel.** R. H. McMILLEN (*J. Ind. Eng. Chem.*, 1913, 5, 123—125).—Two electric furnaces capable of maintaining a temperature of 2500°, and fitted with quartz tubes, are connected up in series, a U tube containing phosphoric oxide being placed between them. The first furnace is connected to the source of pure hydrogen, and the quartz tube contains several spirals of platinum gauze, so that any oxygen contained in the hydrogen is burnt up, the water produced being absorbed in the phosphoric oxide tube. The sample to be analysed (25 grams of drillings) is contained in a porcelain boat in the tube of the second furnace, and the water formed by the reduction of the oxides in the sample is absorbed in a weighed phosphoric oxide U tube attached to the furnace. The latter U tube is guarded by a sulphuric acid wash-bottle.

The usual precautions are taken for sweeping all air and moisture

out of the apparatus before the estimation is commenced. It is advisable to run a blank experiment from time to time.

The results of the analyses of a number of irons and steels are given.  
T. S. P.

**Direct Estimation of Oxygen in Organic Compounds.** MAITLAND C. BOSWELL (*J. Amer. Chem. Soc.*, 1913, 35, 284—290).—A method is described for the direct estimation of oxygen in carbon compounds. The substance, contained in a silica boat, is placed at one end of a quartz tube, 13 mm. in internal diameter and 980 mm. long, which is put into an ordinary combustion furnace. The substance is heated strongly in a current of pure hydrogen, and the products are passed over a long layer of fragments of charcoal, about 1 cu. mm. in size, maintained at a white heat. By this means all the oxygen in the compound is converted into water, carbon dioxide, and carbonic oxide. The water is absorbed in concentrated sulphuric acid, the carbon dioxide in soda-lime, and the carbonic oxide is estimated by passing the gas, freed from water and carbon dioxide, through iodine pentoxide, and absorbing the resulting carbon dioxide with soda-lime (compare Levy, A., 1912, ii, 203). Experiments are quoted which show that the method is capable of giving results of about the same degree of accuracy as the usual combustion method for estimating carbon and hydrogen.  
E. G.

**Iodometric Estimation of Persulphuric Acid.** ERICH MÜLLER and HORST VON FERNER (*Zeitsch. anal. Chem.*, 1913, 52, 195—197).—A stoppered flask holding 100—120 c.c. is filled with carbon dioxide gas. 5 grams of potassium iodide are added, and also 10 c.c. of ferrous sulphate solution (3 grams of crystals, 1 c.c.  $N/2$ -sulphuric acid up to 100 c.c. of water); any iodine liberated is removed with thiosulphate. After adding either the persulphate in powder or in solution and more water so as to leave about 30 c.c. space, the flask is closed and left for five minutes. The iodine liberated, which represents the persulphuric acid, is then titrated with standard thiosulphate. Towards the end, a current of carbon dioxide is passed and the titration continued.  
L. DE K.

**Application of Devarda's Method in the Estimation of Nitrogen in Nitrocelluloses.** KOEHLER, M. MARQUYROL and JOVINET (*Ann. Chim. anal.*, 1913, 18, 45—47).—A combination of the methods of Devarda and of Busch. 0.7 Gram of nitrocellulose is placed into a 700 c.c. flat-bottomed Jena flask, moistened with a little alcohol, and then treated with 30 c.c. of hydrogen peroxide (12 vols.), 60 c.c. of water, and 50 c.c. of aqueous potassium hydroxide, D 1.3; after placing on a small funnel, the flask is heated in a water-bath at 50—60° with frequent shaking. When the nitrocellulose has dissolved (the liquid should not turn yellow), the contents are boiled over the free flame until evolution of oxygen ceases.

When cold, 5 c.c. of alcohol and 2.5 grams of Devarda's alloy

45% aluminium, 50% copper, 5% zinc) in fine powder are added. The flask is connected immediately with a Wagner distilling arrangement, the end of which, drawn to a point, dips into standardised sulphuric acid. When the evolution of hydrogen has finished, the contents are heated just to boiling for twenty minutes, when a stronger heat is applied so as to distil half the liquid within thirty to thirty-five minutes.

The ammonia is then calculated as usual by titrating the excess of sulphuric acid in the receiver.

L. DE K.

**Methods of Estimating Nitrogen in Humus.** CHARLES B. LIPMAN and H. F. PRESLEY (*J. Ind. Eng. Chem.*, 1913, 5, 143—144).—The authors have compared the various methods for the estimation of nitrogen in humus. The humus extract was boiled with magnesium oxide until no more ammonia was evolved, and the nitrogen then estimated in the residue by the methods of Wilfarth, Gunning-Atterberg, and Hibbard, and the salicylic acid method. The Hibbard method was found to be the most satisfactory, giving the highest amounts of nitrogen, the best agreement between duplicates, and the least trouble in manipulation, as well as being the most speedy. It consists in heating the substance with 30 c.c. of concentrated sulphuric acid until fumes of sulphur trioxide are given off, and then adding 12 grams of a salt mixture made in the proportions of 10 grams of potassium sulphate, 1 gram of ferrous sulphate, and 0.5 gram of copper sulphate (compare *ibid.*, 1910, 2, 463). The remainder of the estimation is as usual.

T. S. P.

**Colorimetric Estimations in Water Analysis by means of the Autenrieth-Koenigsberger Colorimeter.** WILHELM AUTENRIETH and ALBERT FUNK (*Zeitsch. anal. Chem.*, 1913, 52, 137—167).—The above colorimeter (*A.*, 1910, ii, 910) is recommended for use in water analysis in the estimation of ammonia, nitrous and nitric acid (and their admixtures), iron, lead, and hydrogen sulphide. The usual reactions are employed. L. DE K.

**Estimation of Ammonia in Effluents and Sewage.** SERGIUS KRAPIVIN (*Zeitsch. anal. Chem.*, 1913, 52, 198—199).—One hundred c.c. of the water are placed in a 200 c.c. flask, 10 c.c. of 10% barium chloride solution are added, and then 10 c.c. of *N* 5 sodium hydroxide and a few drops of phenolphthalein. After diluting to the mark and shaking, the solution is filtered, and 100 c.c. of the filtrate are neutralised with *N* 10 hydrochloric acid; 5 c.c. of 40% formaldehyde are added, and the liquid is titrated with *N* 20 sodium hydroxide until the colour remains pink. The acidity due to the formaldehyde itself is found by adding another 5 c.c. and titrating again.

The acidity liberated on adding formaldehyde represents the ammonia.

L. DE K.

**The Rate of Reaction of Nitrous Acid and Carbamide in Dilute Solutions.** WALTER D. BONNER and EDWIN S. BISHOP (*J. Ind. Eng. Chem.*, 1913, 5, 134—136).—It is shown that nitrous acid

and carbamide react at an appreciable rate, even when the initial concentrations are as low as 0.1 part of nitrite nitrogen per million, the carbamide being present in equivalent amount. If, however, the Griess reagent (sulphanilic acid- $\alpha$ -naphthylamine) is added to the solution, carbamide, even when present in excess, will not react with the nitrous acid, since the reaction between the nitrous acid and the Griess reagent is much quicker than that between the acid and carbamide.

The observation has been made that in very dilute solution carbamide and nitrous acid sometimes fail to react, for no apparent reason.

T. S. P.

**Soluble Silicic Acid in Basic Slag and its Effect on the Estimation of the Phosphoric Acid Soluble in Citric Acid.** MAX POPP, J. CONTZEN, H. HOFER, and H. MENTZ (*Landw. Versuchs Stat.*, 1913, 79-80, 229-278).—The inconvenience caused by the presence of silica in estimating the soluble phosphoric acid in basic slag only occurs in the case of slags deficient in soluble iron. The following method gives satisfactory results: The citric acid extract (50 c.c.) is treated successively with 25 c.c. of iron citrate solution, 10 c.c. of 0.3% hydrogen peroxide, and 25 c.c. of magnesia mixture. The process is completed in the usual manner.

The iron citrate solution is prepared by adding 30 grams of ferric chloride dissolved in 50 c.c. of water to 1000 grams of citric acid; 4000 c.c. of 20% ammonia are then added slowly and carefully until all is dissolved. The volume of the mixture is made up to 5 litres, after which it is filtered.

The magnesia mixture is prepared by dissolving 550 grams of magnesium chloride and 700 grams of ammonium chloride in about 2 litres of water, adding 1750 c.c. of 20% ammonia, and diluting to 10 litres. It is filtered some days afterwards.

The total phosphoric acid in Wolter phosphate is estimated by dissolving 1 gram in 100 c.c. of 3% hydrochloric or nitric acid. The solution (not filtered) is treated with 2 c.c. of 3% hydrogen peroxide and 48 c.c. of iron citrate solution. It is then filtered, and 75 c.c. of the filtrate (=0.5 gram) treated with 25 c.c. of magnesia mixture.

N. H. J. M.

**The Test for Arsenic with Bettendorff's Reagent.** LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1913, 26, 143-144).—It is usually stated that Bettendorff's reagent, when testing for arsenic in solutions containing sulphuric acid, must be used in the cold, as otherwise the stannous chloride reduces the sulphuric acid to hydrogen sulphide, and stannous sulphide is precipitated. The author finds that this is not the case, and heat may be applied. The reagent is best made as follows: 100 grams of clear crystals of stannous chloride are dissolved in sufficient 36-38% commercial hydrochloric acid to give 1000 c.c. of solution. Traces of arsenic in the acid are deposited on keeping, the deposition being accelerated by shaking the solution with 1 gram of finely powdered glass. The clear, supernatant solution is used for the test. In testing

for arsenic one volume of the solution to be tested is heated to boiling with 5 volumes of the reagent, and then left for half-an-hour. Concentrated sulphuric acid must first be diluted with an equal volume of water.

The limit of sensitiveness of the test is 0.001 gram of arsenious oxide per litre.

T. S. P.

**An Internally Electrically Heated Combustion Tube for Organic Analysis.** J. MARER (*J. pr. Chem.*, 1913, [ii], 87, 287-288).—It has been shown previously (A., 1912, ii, 297) that the combustion of organic substances may be carried out without the use of an oxygen-carrier, provided that the combustion tube is strongly heated. In the present communication the author gives a sketch and description of an electrically heated combustion tube, in which the heating is effected internally by means of a spiral of platinum wire fused into the tube itself.

F. B.

**Gas Bubble and Washing Tube for Combustion Apparatus.** H. E. SMITH (*J. Ind. Eng. Chem.*, 1913, 5, 150).—The part of the bubbler containing the sulphuric acid is modified in two ways: (1) a glass stopcock is fused on to the lower part of the bulb, so that the acid can be run out readily; (2) a side-tube containing glass beads is fused on, the top of this tube being closed with a rubber stopper, below which is fused another tube leading to the combustion apparatus. The apparatus can be recharged by taking out the rubber stopper and pouring in acid.

T. S. P.

**Modification of the Parr Total Carbon Apparatus.** C. E. MILLAR (*J. Ind. Eng. Chem.*, 1913, 5, 234-235).—The modification consists in the adaptation of a compensator for changes in temperature and pressure during the measurement of gas volumes, and may be applied to any gas burette. The principle is exactly the same as that applied to the ordinary nitrometer, where a third tube containing a fixed quantity of air is added and put into communication with the mercury of the levelling tube. In reading volumes of gas in the burette, the levelling tube is always raised until the mercury in the compensator stands at a fixed mark, whereby changes of pressure and temperature during the measurements are automatically compensated for.

T. S. P.

**A Method of Examination of Fermentation Gases.** WALTER FRIEDER (*Centr. Bakt. Par.*, 1913, ii, 36, 438-443).—A modification of the method proposed by Burri and Diiggeli (A., 1909, ii, 356). In the original method a shake culture with saccharine agar is prepared at the closed end of a long glass tube, the culture medium being covered by a layer of non-saccharine agar. By the formation of gas the latter is pushed towards the mouth of the tube, and the total gas production may be measured off. For the examination of the gases, the tube is filled with water, and the agar broken up by means of a bent wire; sodium hydroxide is then introduced, and the carbon dioxide absorbed.



This method is open to objection on account of the possibility of appreciable quantities of gas being absorbed or enclosed by the agar medium, and the author suggests (1) that mercury should be employed instead of water for filling the fermentation tube, and (2) that the culture tube filled with mercury should be heated for fifteen to thirty minutes in steam in order to melt the agar and to liberate the gases retained by it. On cooling, the volume of gas may be read off, and sodium hydroxide introduced in the usual manner.

H. B. H.

**A Comparison of Some Qualitative and Quantitative Methods for Carbonates in Soils.** E. W. GAITHER (*J. Ind. Eng. Chem.*, 1913, 5, 138—143).—The author confirms the method given by Marr (A., 1909, ii, 938) for the estimation of carbonates in soils.

If properly made, the litmus paper test is the best qualitative test for the presence or absence of native carbonates in soils from humid regions. Some soils may give alkaline aqueous solutions, because of the hydrolysis of minerals present in the soil. If there are no alkalis or basic materials in a soil which are capable of giving alkaline solutions, their absence will be indicated by the reddening of blue litmus paper.

T. S. P.

**Estimation of Hardness of Waters.** PAUL ROHLAND (*Zeitsch. anal. Chem.*, 1913, 52, 200—201).—The author explains the lathering of the soap solution after the calcium has been precipitated by the marked colloidal character of soap solutions.

L. DE K.

**Control of the Purification of Boiler Feed Water.** GEORG WEISSENBARGER (*Zeitsch. angew. Chem.*, 1913, 26, 140—143).—The author discusses the various methods which have been suggested for the control of the purification of boiler feed water, both from the point of view of accuracy and of time necessary for the analysis, and then proposes the following method: 100 c.c. of the water, at room temperature, are titrated with acid after the addition of 10 drops of a 20% solution of sodium chloride, using 2 drops of a phenolphthalein solution (1 gram in 100 c.c. of 95% alcohol as indicator). The addition of the sodium chloride is to suppress the dissociation of the sodium carbonate, otherwise the end-point with phenolphthalein is affected. Two drops of methyl-orange (1 gram in 1 litre) are then added, and the water again titrated with acid. The neutral solution is then titrated with soap solution of such strength that for 100 c.c. of water, 1 c.c. of the soap solution corresponds with 2° of hardness. A table is given from which, using the titration results, the quantities of lime water or sodium carbonate solution necessary for purification may be directly ascertained.

T. S. P.

**Estimation of Potassium by the Cobaltinitrite Method.** J. L. M. VAN DER HORST VAN DEN BOS (*Chem. Weekblad*, 1913, 10, 182—186).—A description of a method of estimating potassium volumetrically by means of sodium cobaltinitrite, applicable either

to an individual potassium salt, or to a mixture of potassium and sodium salts. The precipitate has the formula  $K_2NaCo(NO_2)_6$ .

A. J. W.

**Estimation of the Carbonates and Hydroxides of Potassium and Sodium when together in Solution.** W. A. BRADBURY and F. OWEN (*Chem. News*, 1913, 107, 85—86).—A measured volume of the solution is titrated with sulphuric acid, using phenolphthalein as indicator. The acid used is equivalent to all the hydroxide and half the carbonate; methyl-orange is now added, and the titration completed; the additional amount of acid used is equivalent to half the carbonate, so that the amount of acid required for the carbonates and for the hydroxides can be calculated from these figures. The fully neutralised solution is evaporated to dryness, and the residue of sulphates weighed. The results obtained give all the data necessary for the calculation of the respective amounts of carbonates and hydroxides present.

Attempts to carry out the estimation by evaporating the solution to dryness and extracting the hydroxides with absolute alcohol gave unsatisfactory results.

T. S. P.

**Estimation of Alkalis in Rocks.** H. V. KUSHNAYYA (*Chem. News*, 1913, 107, 100—101).—A suitable quantity of the powdered sample is heated in a platinum dish with hydrofluoric and sulphuric acids, and after expelling the excess of acid, the residue is dissolved in boiling dilute hydrochloric acid; any undissolved matter must be again submitted to the treatment with hydrofluoric and sulphuric acids. The mixed filtrate is then made up to a definite volume, and an aliquot part, representing 1 gram of the sample, is withdrawn. After evaporating to dryness and igniting the residue, thus rendering the iron and alumina insoluble, the alkali sulphates are extracted with boiling water, and, without filtering, converted into chlorides by adding barium chloride solution; some barium hydroxide is also added.

After removing the excess of barium with ammonium carbonate, the alkali chlorides are weighed jointly as usual. The potassium is then estimated as platinumchloride in the ordinary manner.

L. DE K.

**Estimation of the Absorbed Bases in Soils.** DMITRI N. PRAMISCHNIKOV (*Lening. Versuchs-Stat.*, 1913, 79-80, 667—686).

Kellner's method of estimating the absorbed bases in soils (displacing with ammonium chloride) is both slow and difficult, as the ammonium chloride is not easy to remove. Ammonium nitrite acts with greater vigour than the chloride, but has the disadvantage of being unstable. Both ammonium acetate and 3.2% ammonia are suitable for ascertaining the amount of absorbed potassium.

For estimating ammonia in soils, it was found that by digesting the soil (200 grams) ten times with 5% potassium chloride and distilling with magnesia, results were obtained which agree most nearly with those obtained by Boussingault's method and by

Schloesing's hydrochloric acid method. The sodium hydroxide method of Schloesing gives results which are evidently too high owing to the decomposition of amido-compounds.

Previous experiments showed that whilst plants can assimilate the potassium of biotite, nepheline, and muscovite, the potassium of orthoclase, sanidine, and leucite is not available, or only to a very slight extent. It was found that by extracting the minerals once with ammonium chloride, and estimating the potassium dissolved, similar indications were obtained.

Experiments with barley showed that the potassium of zeolites is almost completely unavailable when isolated. In contact with nutritive salts, and even with calcium carbonate, it is readily assimilated.

N. H. J. M.

**The Gay-Lussac Method of Silver Estimation.** FREDERIC P. DEWEY (*J. Ind. Eng. Chem.*, 1913, 5, 209—214).—An account of the method used and the precautions taken in the United States Mint for the estimation of silver according to the method of Gay-Lussac. Very elaborate tests of the method have been made, and the conclusion arrived at is that two analysts, working on identical samples of standard silver and making four estimations each, may differ as much as 1 "fine" (0.1%) in their reports. T. S. P.

**New Forms of Flask and Beaker for the Volumetric Estimation of Silver, Chlorine, Sulphuric Acid, etc.** V. N. IVANOV (*J. Russ. Phys. Chem. Soc.* 1913, 45, 66—69\*).—Volhard's method gives results which are about 0.1% too high (or too low) when used for the estimation of silver (or chlorine). This inaccuracy, which is due to adsorption of ammonium thiocyanate by the silver thiocyanate, may be avoided by using for the titration a beaker with vertical or slightly tapering sides, and a concave base. The central part of the base is blown into the form of a spherical bulb, which juts up into the body of the beaker, and leaves a distance of not more than 0.5 cm. between itself and the main wall of the beaker. The precipitate formed falls through this narrow space to the bottom of the beaker, where it remains even after rotation of the vessel. When the end-point is approached, the contents of the beaker are thoroughly mixed by vigorous shaking, the precipitate being allowed to settle again before the titration is continued. The final coloration is found to persist for some hours, whereas that obtained in the ordinary way disappears in the course of a few minutes. The above procedure yields results identical with those given by Melsch's volumetric method or by the gravimetric method. T. H. P.

**Purification of Barium Sulphate Precipitated in the Estimation of Barium.** FRANK A. GOUGH and D. C. HILL (*Amer. J. Sci.* 1913, [iv], 35, 311—314). When barium is estimated by precipitation of the sulphate in presence of alkali salts, considerable errors may be occasioned by the occlusion of foreign substances. These may be avoided by dissolving the precipitate in concentrated sulphuric acid and evaporating to dryness, when the barium sulphate

\* and *Chem. Zeit.*, 1913, 37, 127.

crystallises in more or less coarsely granular crystals, which can be readily washed free from the alkali metal sulphates.

The evaporation of the sulphuric acid solution can be effected in a platinum crucible heated by a Hempel burner, or by directing a small blow-pipe flame to the tip of a cone of fine platinum gauze, which is fitted into the mouth of the crucible. The use of this gauze cone is quite effective in preventing loss by sputtering.

H. M. D.

**Estimation of Copper in White Metal Alloys.** FREDERICK JENKINSON and L. ATTCHISON (*Chem. News*, 1913, 107, 121).—0.5 Gram of drillings is dissolved in 10–15 c.c. of aqua regia, and an equal volume of water is added. Any lead chloride separating on cooling is filtered off. To the filtrate is added 1 gram of tartaric acid, and the bulk of the acids is neutralised with sodium hydroxide. The heated liquid is then poured slowly into a boiling solution composed of 20 grams of sodium hydroxide and 2–3 grams of hydrazine hydrochloride in 250–300 c.c. of water. After fifteen minutes the metallic copper is collected on paper pulp, washed with hot water, and then redissolved in dilute nitric acid (1 acid of D 1.2–1 water). The solution is evaporated to pasty constituency, and the residue is moistened with a few drops of nitric acid and dissolved in water; the solution should not be opalescent (absence of tin). After rendering alkaline with solution of sodium carbonate, acetic acid is added in slight excess, and the solution boiled. When cold, the copper is titrated in the usual way, iodometrically. L. DE K.

**The Thiocyanate Permanganate Method for Copper in Ores.** D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1913, 5, 215–216).—Gues's method for the estimation of copper (compare Grossmann and Hölter, A., 1909, ii, 449) is modified by oxidising most of the thiocyanate with alkaline permanganate and completing the oxidation with acid permanganate; a correction factor is thereby avoided.

The weight of ore taken should contain from 0.05–0.3 gram of copper. It is heated for several minutes with 5 c.c. of concentrated hydrochloric acid, after which 10 c.c. of nitric acid are added, and the ore digested until completely decomposed; 10 c.c. of sulphuric acid (1:1) are added, and the whole evaporated until sulphuric acid fumes appear. It is then cooled, 50 c.c. of water containing 3 grams of tartaric acid added, and heated until all soluble salts are dissolved; again cooled, ammonia added until the liquid is a deep blue, and then acidified with sulphuric acid. After the addition of 1 gram of sodium sulphite, dissolved in 20 c.c. of water, the solution is heated nearly to boiling, and then a solution of 1 gram of potassium thiocyanate in 20 c.c. of water added, with vigorous stirring, to precipitate the copper. It is heated for some time to coagulate the precipitate and dissolve the tartaric acid, filtered through a Gooch crucible, washed well, and then 30 c.c. of a hot 10% solution of sodium hydroxide run through the crucible in order to decompose the cuprous thiocyanate; and again washed well. The filtrate is warmed to 50°, and the thiocyanate present titrated with

permanganate, spot-testing it from time to time with ferric chloride and hydrochloric acid. When the red colour in the spot test becomes very faint, 30 c.c. of sulphuric acid (1:1) are added, all the manganese dioxide allowed to dissolve, and the titration finished with permanganate.

No elements interfere with the method except silver; any lead present is collected as sulphate after evaporating with sulphuric acid. The results are accurate.

T. S. P.

**Electrolytic Estimation of Copper in Ores containing Arsenic, Antimony, or Bismuth.** D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1913, 5, 216).—Advantage is taken of the fact that copper is entirely precipitated as cuprous thiocyanate from a solution containing ammonium sulphate, ammonium tartrate, and tartaric acid. The ore (1 gram, or more if the sample is low in copper) is treated according to the method given in the preceding abstract, using, however, 7 c.c. each of hydrochloric acid and nitric acid, 5 c.c. of sulphuric acid, 30 c.c. of water, and 2 grams of sodium sulphate. The precipitate of cuprous thiocyanate, after being collected on a dense filter, is washed several times with a solution containing about 1% of potassium thiocyanate, and the same amount of tartaric acid. The precipitate is then dissolved in nitric acid (1:2), using as little as possible, the solution boiled to destroy all the thiocyanate, the volume made up to 125 c.c., and the copper estimated electrolytically.

T. S. P.

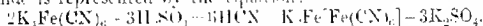
**The Electro-analytical Separation of Copper from Tungsten and Molybdenum.** W. D. TREADWELL (*Zetsch. Elektrochem.*, 1913, 19, 219-221).—It is shown that tungsten and molybdenum are not quantitatively separated from copper by electrolysis in potassium cyanide solution. Copper, existing as chloride, nitrate, sulphate, phosphate, or acetate, can be quantitatively separated from tungsten, which must be present as sodium tungstate, by the following process. The solution is treated with 15-20 c.c. of concentrated ammonia and 3-5 grams of ammonium sulphate, and electrolysed with current having an *E.M.F.* of 2 volts. Stationary or rotating cathodes may be used, and there is no deposition of tungsten if the current is allowed to pass for long periods after all the copper has been deposited. Copper can be separated from molybdenum, which must be present as ammonium molybdate by adding an excess of sulphite to the ammoniacal solution, and electrolysing with current having an *E.M.F.* of 0.9 volt. In this process the current must not be allowed to flow for more than a few minutes after the blue colour has disappeared from the solution. Experiment shows that if it is allowed to flow for five minutes after the blue colour has vanished, all the copper will have been deposited, and the molybdenum hydroxide will have been precipitated. It is also stated that in the quantitative estimation of molybdenum as molybdenum trioxide, it must not be heated above 100°C., and the operation must be carried out in a porcelain crucible, and not

in a platinum crucible. The reasons for these precautions are: (1) molybdenum trioxide is volatile above  $450^{\circ}$ , and (2) it is reduced in contact with platinum.

J. F. S.

**Estimation of Free Acid or Base in Aluminium Sulphate.**  
V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 57-66).—The method usually employed for the estimation of free acid in aluminium sulphate is that devised by Beilstein and Grosset, which consists in addition of ammonium sulphate to form ammonium alum, treatment with alcohol, evaporation of the filtrate to dryness, and titration of the dissolved residue with alkali in presence of methyl-orange. The author finds, however, that this method indicates about 0.22% of free sulphuric acid after addition to the aluminium sulphate of a quantity of alkali five times as large as should be sufficient to neutralise the free acid originally found. Further, the result obtained varies with the amount of water taken to dissolve the aluminium sulphate, and with the amount of alcohol used to wash the precipitated alum.

The following method is free from these defects. One gram of the sulphate is dissolved in a 100 c.c. Erlenmeyer flask in 50 c.c. of water, and into the liquid, heated to  $85^{\circ}$ , 12 c.c. of potassium ferrocyanide solution (1:12) are quickly added, with constant stirring, from a burette. Immediately afterwards 20 c.c. of barium chloride solution (1:19) are pipetted into the liquid, which is kept in vigorous movement. The whole of the liquid and precipitate is introduced into a 100 c.c. flask, and the volume made up to 100.25 c.c., 0.25 c.c. representing the volume displaced by the precipitate. When mixed, the contents are allowed to settle for an hour, 25 or 30 c.c. of the clear supernatant liquid being then titrated with decinormal sodium hydroxide solution in presence of 3 or 4 drops of methyl-orange solution (1:1000). The method has been tested by means of a solution of aluminium sulphate, to which different known proportions of sulphuric acid were added, and found to give satisfactory results. The reaction with the ferrocyanide is represented by the equation:



When the clear liquid from the barium precipitate exhibits no acidity, the substance contains free base. In such case, to a solution of 1 gram of the aluminium sulphate in 50 c.c. of water are added 2 c.c. of seminormal hydrochloric acid, the liquid being then heated to  $85^{\circ}$ , and treated as described above. The difference between the amount of acid then found and that corresponding with 2 c.c. of seminormal acid is calculated as either aluminium hydroxide or sodium hydroxide.

If a rapid but not very accurate estimation of the acidity is desired, the aluminium sulphate solution may be titrated immediately with seminormal alkali hydroxide solution, a drop of the liquid being removed from time to time and placed on a filter paper previously soaked in methyl-orange solution (1:1000) and dried. When the red colour originally formed round the precipitate gives

place to an orange colour, the titration is complete. This procedure gives results about 0.2% too low. T. H. P.

**Rapid Estimation of Manganese in the Presence of Iron.** M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1913, 18, 56—58).—The solution containing the manganese is heated to boiling and precipitated with excess of sodium hydroxide and about 1 gram of persulphate. The precipitate, after being washed, is heated in a special apparatus (very much like that of Baubigny and Chauvanne; A., 1904, ii, 203) with hydrochloric acid, and the vapours are absorbed in a solution containing 3 grams of potassium iodide, 5 grams of sodium acetate, and 4—5 grams of zinc oxide in suspension. A slow current of carbon dioxide facilitates the elimination of the chlorine.

The iodine liberated is then titrated as usual with  $N/10$  thio sulphate; 1 c.c. = 0.000275 gram of metallic manganese. L. DE K.

**The Volumetric Estimation of Manganese in Rock, Slags, Ores, and Spiegels.** FLOYD J. METZGER and L. E. MARRS (*J. Ind. Eng. Chem.*, 1913, 5, 125—126).—The application of the authors' method for the estimation of manganese (A., 1912, ii, 94) to rock, slags, etc., is given.

Two to five grams of rock are boiled in a platinum dish with 5—15 c.c. of dilute sulphuric acid (1:2), and then with 5—15 c.c. of hydrofluoric acid until decomposition is complete; 5—10 c.c. of dilute nitric acid (1:1) and 2—3 c.c. of concentrated sulphuric acid are added, the flame removed, and about 1 gram of ammonium persulphate added in small portions at a time. When evolution of gas has ceased, the solution is evaporated until fumes of sulphur trioxide appear, cooled, 50 c.c. of water added, boiled and cooled. It is then transferred to a waxed beaker, and treated as described in the previous paper (*loc. cit.*). Slag is treated similarly to rock. 0.2—1.0 gram being taken. Ores (pyrolusite) are dissolved in 50% hydrochloric acid, the solution evaporated down with sulphuric acid, nitric acid then added, and afterwards ammonium persulphate, the remainder of the treatment being similar to that with rock. 0.5—1 Gram of the ore is taken. Ores, slags, etc., which are insoluble in hydrochloric or nitric acid, are treated in the same way as rock. Spiegels and ferromanganese are analysed according to the method already given (*loc. cit.*). T. S. P.

**The Estimation of Small Quantities of Manganese and Chromium in Minerals and Rocks.** MAX DIETRICH (*Zentral. anorg. Chem.*, 1913, 80, 171—173).—The colorimetric estimation of manganese in rocks is often difficult, owing to the presence of chromium, which alters the colour of the permanganic acid solution. By adding ammonia to the mixed solution of permanganate and chromate and warming, all the manganese and iron are precipitated as hydroxides. The washed precipitate may be dissolved, warmed, and oxidised by means of ammonium persulphate as usual. The chromium may be estimated colorimetrically by comparison with a

standard solution of potassium chromate after removal of silver by sodium chloride, and concentration. The method is not accurate for chromium when the quantity of this falls below 2 mg.

C. H. D.

**Volumetric Estimation of Chromium, Vanadium, and Iron in Presence of One Another.** FREDERICK W. ATACK (*Analyst*, 1913, **38**, 99—102).—A solution of methylene-blue (4 grams per litre) is boiled with dilute hydrochloric acid in a current of carbon dioxide, and then decolorised with titanous chloride. A known quantity of the solution of the above metals is then run in, and the regenerated blue titrated with titanous chloride.

Chromium must be converted into chromate by boiling with sodium peroxide. If iron is also present, dilute sulphuric acid is added until the precipitate is redissolved; the result then will be chromate + ferric salt. By boiling another portion of the solution with hydrochloric acid, thus reducing the chromic acid, a second experiment will give the iron only. Vanadium, either alone or in presence of iron, is estimated as directed for chromium.

In a mixture of the three metals, one portion is titrated as directed, the result being the amount of chromate, vanadate, and ferric salt. A second portion is boiled with hydrochloric acid, thus, when titrated, giving the ferric salt only. A third portion is boiled with sulphur dioxide and then (partly) reoxidised with permanganate. The result of the methylene-blue titration is then vanadate + ferric salt.

In iron alloys the chromium may be determined directly by fusion with sodium hydroxide and peroxide. The chromate formed is then extracted with water.

L. DE K.

**An Electrolytic Method for the Estimation of Tin in Canned Food Products.** ALLERTON S. TISHMAN and EVERETT R. WETTENGEL (*J. Ind. Eng. Chem.*, 1913, **5**, 217—218).—The usual method employed in the authors' laboratories was to destroy the organic matter with a mixture of sulphuric and nitric acids, neutralise the solution, from which all nitric acid had been expelled, with ammonia, acidify with hydrochloric acid, precipitate the tin as sulphide, and weigh as oxide. The great objections to this method are the time involved, the quantities of acid used, and the damage caused to the hoods and flues by the acid fumes. The method now adopted is as follows: 50 grams of the pulped material are brought to a slow boil with 50 c.c. of concentrated hydrochloric and 25 c.c. of nitric acid, using a 600 c.c. beaker. The boiling is continued for five minutes, stirring continuously, unless foaming occurs, when the flame is removed, and the material allowed to digest for ten minutes. The solution is then diluted with an equal volume of water, made alkaline with strong ammonia, and 25 c.c. of saturated ammonium sulphide, digested for a few minutes, and then filtered through a fluted filter. The residue is washed with boiling water containing a little



ammonium sulphide, and the tin in the filtrate (400 c.c.) is deposited on a rotating cathode. The deposition of tin is complete in one to four hours. 1.5 Amperes at 4 volts are used, but no details are given of the area of the cathode, which consists of a platinum crucible. T. S. P.

**Estimation of Tin in Bronzes.** FREDERICK LEBBETSON and L. ARCHISON (*Chem. News*, 1913, 107, 109--110).—The tin is estimated directly in the precipitated metastannic acid, without any previous ignition or weighing.

For a bronze containing about 10% of tin, 1 gram of coarse drillings is taken and treated with 10--15 c.c. of nitric acid ( $D=1.4$ ). (The quantity of alloy taken should be such that it contains about 0.1 gram of tin.) When the action is complete, the solution is evaporated to a paste, 75 c.c. of water added, and boiled for a few minutes. The precipitate is allowed to settle, and washed by decantation through a tightly-packed filter of asbestos pulp, the hot wash-water containing a small quantity of nitric acid. It is washed finally with water until the free nitric acid is removed, and the whole of the filter and precipitate then transferred to the flask containing the greater portion of the metastannic acid, using as little water as possible in the transference (less than 20 c.c. if possible). Next a volume of concentrated sulphuric acid is added equal to that of the water used, and the solution boiled for three minutes, taking due precautions against bumping. Then 50 cc. of concentrated hydrochloric acid are added and boiled for two minutes, when a clear solution should be obtained. About 1 gram of finely powdered antimony is added, boiled for about a minute, and then cooled rapidly under the tap in an atmosphere of carbon dioxide. When quite cold, it is titrated at once with  $N/20$  iodine, using starch as indicator. The proportion of sulphuric acid to hydrochloric acid used should be about 3:5 by volume; a greater proportion of sulphuric acid interferes with the method. Dilution of the solution has no ill-effect on the titration, and the asbestos interferes in no way, the end-point being quite sharp.

The following method is based on the use of hydrazine for the precipitation of copper (compare Jannasch and Biedermann, A. 1900, ii, 315). 0.5 Gram of the drillings is dissolved in 10 c.c. of aqua regia, and the solution diluted with an equal volume of water, most of the free acid neutralised with a solution of sodium hydroxide, taking care that no precipitate is formed, and heated to boiling. In a large, conical flask a solution of 20 grams of sodium hydroxide in 300 c.c. of water is heated to boiling, 2--3 grams of hydrazine hydrochloride added (not sulphate), and then the solution of copper and stannic chlorides is run in drop by drop, shaken vigorously meanwhile. After digesting for fifteen minutes, the precipitated copper is collected, and washed with hot water. The filtrate is concentrated, acidified with hydrochloric acid, and the tin estimated either by the method above described, or gravimetrically. The copper can be estimated by any of the usual methods. T. S. P.

**Volumetric Estimation of Tin by means of Potassium Bromate.** FRITZ FICHTER and E. MÜLLER (*Chem. Zeit.*, 1913, **37**, 309).—Stannous chloride solutions may be titrated with potassium bromate solution, provided that the solution contains a sufficient quantity of free acid (compare A., 1902, ii, 12), the end-point of the titration being denoted by production of a yellow coloration due to the liberation of free bromine on the addition of bromate solution after all the stannous chloride has been oxidised. Twenty c.c. of a solution of a tin salt are treated with a small quantity of aluminium wire, and, when the aluminium has dissolved, 30 c.c. of concentrated hydrochloric acid and 20 c.c. of water are added, and the mixture is heated until the precipitated tin has redissolved. The solution is then cooled and titrated with a standardised potassium bromate solution. W. P. S.

[Assay of] Alloys of Tin and Antimony. POSTIO (*Ann. Chem. anal.*, 1913, **18**, 47—48).—In the practical absence of copper, 0.5 gram of the alloy is oxidised with nitric acid (D 1.3), the tin and antimony oxides are washed with acidified water, heated to bright redness, and weighed. The antimony is then estimated separately in another 0.5 gram of the sample by evaporation with nitric acid, moistening the residue with 1 c.c. of strong sodium hydroxide solution, and heating, short of boiling, with 60—75 c.c. of sodium monosulphide (D 1.15). From the solution obtained the antimony is then precipitated electrolytically (0.3 ampere, 4 volts) after first adding 20 c.c. of 20% potassium cyanide. The antimony is then removed from the platinum gauze cylinder with nitric acid, and finally converted by ignition into oxide.

In presence of copper, the joint oxides of tin and antimony are obtained pure as follows: 0.5 gram of the alloy is heated with hydrochloric acid and a sufficiency of nitric acid, the liquid is evaporated to 5 c.c., and after adding 50 c.c. of nitric acid (D 1.3) the whole is boiled until red fumes cease to be evolved. At short intervals a few grams of potassium chlorate are then added, and the whole is kept boiling for some twenty minutes. After adding an equal volume of water and allowing to deposit, the mixed oxides are collected, washed with acidified water, ignited, and weighed.

L. DE K.

**Assay of Commercial Vanadic Acid.** GABRIEL CHESNEAU (*Ann. Chim. anal.*, 1913, **18**, 108—111).—Moisture and loss on ignition are determined as usual; the latter is often negative. Vanadic acid, silica, iron, manganese, calcium, and magnesium are estimated by fusing 1 gram of the product with 2—3 grams of sodium carbonate containing 10% of nitre. On boiling with water, vanadic acid, silica, and alumina pass into solution, whilst the oxides of iron and manganese remain with the carbonates of calcium and magnesium. The insoluble matter is redissolved in hydrochloric acid, and the solution analysed as usual. Both the iron oxide obtained and the filtrate from the magnesium contain traces of vanadium; from G. iron it may be recovered by fusion as directed, and the

aqueous extract may then be united with the magnesium filtrate and the vanadium estimated colorimetrically with hydrogen peroxide after concentration of the liquid and acidifying with nitric acid.

The alkaline solution is acidified with nitric acid and evaporated to dryness to render the silica insoluble. After treatment with dilute nitric acid, the silica is collected and the filtrate heated with slight excess of ammonia. The precipitate consists of alumina containing perhaps phosphoric or arsenic acid. After ignition and weighing, allowance is made for these acids, also for traces of vanadic acid, which may have co-precipitated. To the filtrate from the alumina is added barium nitrate, which yields a precipitate containing after ignition 37.24% of vanadic acid. Traces of vanadic acid in the filtrate may be estimated colorimetrically. The weight must, however, be corrected for phosphoric acid and arsenic acid, which also form insoluble barium compounds.

Sodium oxide is estimated by the Lawrence Smith method (fusion of 1 gram with 8 grams of calcium carbonate and 1 gram ammonium chloride; an extra addition of 3 grams of barium carbonate is recommended here).

Arsenic and phosphorus: 5 grams of the product are fused with 10 grams of sodium carbonate, the solution is acidified with hydrochloric acid, and the arsenic acid reduced with sulphur dioxide. After boiling, the arsenic is then precipitated as sulphide with hydrogen sulphide. The filtrate is evaporated with addition of 2—3 c.c. of pure sulphuric acid, and after dissolving in water and adding a few grams of ammonium nitrate the phosphoric acid is precipitated by heating for two hours at 40° with an equal volume of molybdate solution. It must be remembered that a portion of this phosphoric and arsenic acids may be contained in the alumina precipitate, and the remainder in the barium compound.

L. DE Z.

**Relationship of Cæsium and Rubidium Salts to the Heavy Metals.** M. WAGENAAR (*Pharm. Weekblad*, 1913, 50, 273—280). The author recommends cæsium chloride for the microchemical detection of bismuth, cadmium, chromium, and zinc; and rubidium chloride for that of antimony, bismuth, aluminium, and chromium.

A. J. W.

**Separation of Columbium and Tantalum by means of Potassium Chloride in Hydrofluoric Acid Solution.** ENG. MERTENBERG and PAUL WISZER (*Zeitsch. angew. Chem.*, 1913, 26, 157—158). Thirty grams of the ore are decomposed by melting with potassium pyrosulphate. The residue is boiled with water and freed from any interfering metals. Of the purified acids, 5—10 grams are taken for the columbium estimation. This is dissolved in a sufficient amount of hydrofluoric acid, and mixed with an excess of saturated solution of potassium chloride. The deposit of potassium tantalum fluoride is collected, heated with sulphuric acid to dryness, and again treated with hydrofluoric acid and potassium chloride. In both cases the deposit is washed with a cold solution of potassium chloride. The

compound is then decomposed by means of sulphuric acid, the tartaric acid is first boiled with water containing hydrochloric acid, then with ammonia, and finally weighed as pentoxide.

The columbium contained in the filtrate is recovered as usual; any titanium present should be estimated colorimetrically and allowed for.

L. DE K.

**The Estimation of Acetylenic and Ethylenic Hydrocarbons in Mixtures of Gaseous Hydrocarbons.** PAUL LEDER and A. DAMIENS (*Compt. rend.*, 1913, 156, 557--559. Compare this vol. ii, 253).—The authors advocate two new reagents for use in gas analysis, one to absorb acetylenic hydrocarbons, and the other to absorb the olefines. The first is a solution containing 25 grams of mercuric iodide and 30 grams of potassium iodide in 100 c.c. of water. When being used, a small fragment of potassium hydroxide is introduced into the absorption tube. It is capable of absorbing twenty times its volume of acetylene, a white precipitate being deposited. The olefines are no more soluble in this reagent than in water.

The second reagent is a 1% solution of vanadium pentoxide in concentrated sulphuric acid, or a 6% solution of uranyl sulphate in the same acid. Either of these solutions can be employed, and will take up one hundred and fifty times their volume of ethylene, whilst being without action on carbon monoxide. The absorption is rapid, due to the presence of the catalyst.

W. G.

**Estimation of Alcohol in Very Dilute Solutions by means of Permanganate.** H. P. BARENBRUNT (*Zeitsch. anal. Chem.*, 1913, 52, 167--172).—Five c.c. of a fermented liquid (wine, beer, etc.), previously diluted so as to contain about 0.2% of alcohol, are poured into a mixture containing 100 c.c. of solution of potassium permanganate (39 grams in 4 litres) and 40 c.c. of aqueous sodium hydroxide (150 grams in 1 litre), which has been heated to boiling. After continuing the boiling for one minute, 100 c.c. of oxalic acid (80 grams in 4 litres) are added, followed by 40 c.c. of dilute sulphuric acid (2:5), and the solution is then titrated with permanganate (5.182 grams of potassium permanganate per litre). The result = excess of oxalic acid (A c.c.).

Meanwhile 5 c.c. of the liquid have been evaporated to dryness on the water-bath, and the residue dissolved in 5 c.c. of a solution of sucrose (1 gram in 250 c.c. of water), and the solution treated as before. Allowance is then made for the reduction caused by the sugar (28.95 c.c. permanganate), and the result (B c.c.) is deducted from A. Multiplied by 0.384, the number of mg. of alcohol, and multiplied by 0.483, the number of cm. of alcohol contained in the 5 c.c. operated on are obtained.

The addition of the sucrose improves the accuracy of the process.

Traces of alcohol in a liquid containing organic matters must be first recovered by distillation before applying the process. A little sucrose added to the distillate and allowed for.

L. DE K.

**Potassium Permanganate in the Quantitative Estimation of Some Organic Compounds.** C. M. PENCE (*J. Ind. Eng. Chem.*, 1913, 5, 218—220).—Tocher's method for the estimation of phenol (A., 1901, ii, 333; compare also Donath and Ditz, A., 1900, i, 137) is open to the objection that the manganese dioxide formed in the oxidation with alkaline permanganate is not readily reduced in the subsequent operations. The method is modified as follows: 25 c.c. of the phenol solution (0.4 gram per litre) are added to 50 c.c. of  $N/10$ -permanganate and 3–4 grams of sodium hydrogen carbonate contained in a 500 c.c. glass-stoppered conical flask. It is boiled for five to ten minutes (with stopper removed), cooled to 60°, acidified with dilute sulphuric acid, and after keeping for two minutes cooled to room temperature. The solution is diluted, 5 c.c. of 20% potassium iodide added, and the liberated iodine titrated with  $N/10$ -thiosulphate in order to determine the excess of permanganate. The phenol is oxidised to carbon dioxide.

Pyrogallol, catechol, resorcinol, quinol, salicylic acid, and salol may be estimated similarly, but the cresols and benzoic acid do not give satisfactory results. T. S. P.

**The Quantitative Estimation of the Oxidation Products of Cholesterol.** ISAAC LAFSCHÜTZ (*Biochem. Zeitsch.*, 1913, 48, 373—417). A method is described by means of which oxycholesterol can be estimated in the unsaponifiable products obtained from tissues and other sources. This substance gives a colour reaction with a mixture of acetic and sulphuric acids, which is readily converted into a pure green colour by the addition of a few drops of 5% ferric chloride solution in acetic acid. Solutions obtained in this way give a spectrum with a well defined band in the red, the breadth of which is proportional to the amount of oxycholesterol in the solution. Three methods of spectroscopic estimation, by means of this band, are described, namely, (a) by a dilution method, in which the solution with unknown amount of oxycholesterol is diluted until it gives the same spectrum as a standard solution; (b) by alteration of the depth of layer of the solution used for absorption, until the spectrum is the same as that of a standard solution. This is the most accurate method, and an instrument constructed by Zeiss, with specially made vessels for altering the depth of the fluids, the absorption spectra of which are to be investigated, are described and figured in the text; (c) by ascertaining the dilution of the fluid necessary to produce the disappearance of the band. As the esters of oxycholesterol do not give the colour reaction, it is possible to estimate these by determining the amount of oxycholesterol present before and after hydrolysis. A method is given for preparing oxycholesterol for standard solutions, in which cholesterol in acetic acid solution is oxidised by benzoyl peroxide. Other oxidation products of acid character are obtained at the same time, of which a preliminary account is given by the author. The actual methods of carrying out the oxycholesterol estimations are given in full detail. S. P. S.

**Influence of Ammonium Sulphate in the Polarimetric Estimation of Lactose.** G. JANSSON-BLOM (*Zeitsch. physiol. Chem.*, 1913, **83**, 441—443).—The presence of ammonium sulphate in such quantity as is used in the preparation of milk for polarimetric observation is shown to diminish the rotatory power of lactose very slightly. A correction of 0.1% is to be applied when the amount of lactose is from 4 to 6%. E. F. A.

**Detection of Invert Sugar by means of  $\beta$ -Naphthol.** FRANZ M. LATTERSCHEID (*Chem. Zeit.*, 1913, **37**, 321).—The test proposed depends on the fact that commercial invert sugar contains traces of furfuraldehyde compounds, which yield a red coloration with concentrated sulphuric acid and  $\beta$ -naphthol. For the detection of invert sugar in honey, 20 grams of the sample are rubbed down in a mortar with successive quantities of ether, the ethereal solutions are filtered, a small crystal of  $\beta$ -naphthol is added to the filtrate, and the ether is allowed to evaporate at the ordinary temperature. The residue is then treated with 5 c.c. of 88–90% sulphuric acid. Natural honey yields a dirty yellow coloration, a faint pink tint being observed in many cases, but if invert sugar is present a distinct red or bluish-violet coloration develops within thirty minutes. The test will readily detect the presence of 5% of invert sugar in honey. W. P. S.

**The Soluble Nitrogenous Substances as a Factor for Valuing Flour.** EUG. ROUSSEAU and MARCEL SIROT (*Compt. rend.*, 1913, **156**, 723—725).—The authors have determined the total nitrogen, and the nitrogen in an aqueous extract of a number of flours, and find that the ratio,  $\frac{\text{total nitrogen}}{\text{soluble nitrogen}}$ , gives a useful indication as to the value of the flour for bread-making. In good flours the mean value of the ratio is 5.72; and if the value falls below 5.20 it is generally a sign of an unsatisfactory flour. This ratio has been found useful in the case of flours which, from ordinary analyses, appeared to be of the same value for bread-making, although differing in actual practice. W. G.

**Estimation of Solid Fatty Acids by Hahn and Mitchell's Method.** ALFRED HEIDESCHKA and A. BRUNER (*Zeitsch. öffentl. Chem.*, 1913, **19**, 87—89).—This method (A., 1897, ii. 289) was found to yield trustworthy results in the case of stearic acid, and also with palmitic acid and myristic acid, alcohol saturated with the respective acids being employed in the last two instances. The results found for palmitic acid are, however, too high if more than 0.5 gram of the acid is taken for the estimation. Whilst the presence of acids which are readily soluble in alcohol does not interfere with the estimation, it is essential that the particular acid under examination should not be mixed with other fatty acids only slightly soluble in alcohol. W. P. S.

**Microchemical Analysis of Plants. III. Detection of Cinnamic Acid, Especially in Resins.** OTTO TRYMANN (*Pharm. Zentr.*, 1913, **54**, 133—136).—The micro-sublimation test described

previously by the author (A., 1912, ii, 104) affords a simple means of detecting and identifying cinnamic acid. When benzoic acid is also present in the substance under examination the sublimate will contain both acids, but it will usually be found that the benzoic acid sublimes before the cinnamic acid; if the sublimate is exposed to the atmosphere for a few days, the benzoic acid will volatilise completely. Cinnamic esters also yield a crystalline sublimate. The cinnamic acid may be distinguished from benzoic acid by several reactions, particularly that with bromine; by exposing the sublimate to bromine vapour, the cinnamic acid forms brownish-yellow droplets, and eventually yields crystals of dibromocinnamic acid. Under similar treatment benzoic acid remains colourless, but the crystals dissolved partially. W. P. S.

**Estimation of Fat in Foods with Special Reference to Extraction with Trichloroethylene.** R. NEUMANN (*Landw. Versuchs-stat.*, 1913, 79-80, 701-736).—Fat can be estimated in all kinds of food by extracting with trichloroethylene; the usual shaking apparatus is employed. Ether dissolves non-fatty substances which are not extracted by shaking for a short time with trichloroethylene. This solvent has the advantages that the substance to be extracted need not be dried, and that it is not inflammable.

The disadvantages are the decomposition of trichloroethylene by light; it can only be used in diffused light, and must be kept in darkness. Owing to its characteristic taste, its removal with a pipette is unpleasant, although not injurious to health. An automatic apparatus is desirable. N. H. J. M.

**Lecithin Preparations and the Estimation of Lecithin.** ROBERT CONN (*Zeitsch. öffentl. Chem.*, 1913, 19, 54-62).—Apart from pure lecithin, there are now on the market preparations, such as pills, tablets, powders, foods, etc., stated to contain definite amounts of lecithin; examination of these preparations shows that in a number of cases the proportion of lecithin present falls short of the amount guaranteed. The following method is recommended for the estimation of lecithin, and consists essentially of the extraction of the lecithin, the purification of the latter, and the estimation of the amount of phosphorus present. From 1 to 2 grams of a lecithin preparation, or from 5 to 20 grams of a food, are extracted with cold alcohol for some hours, then boiled twice for two hours with successive quantities of alcohol, and finally extracted for two hours with boiling chloroform. The alcoholic and chloroform solutions are evaporated, and the residue is boiled for two hours with chloroform, which dissolves the lecithin, whilst free phosphoric acid and glycerophosphoric acid remain insoluble. The chloroform solution is then filtered and evaporated. For the estimation of the phosphorus, this residue may be oxidised by heating with a mixture of sulphuric and nitric acids, or ignited in the presence of magnesium oxide or of a mixture of sodium carbonate and potassium nitrate; the resulting phosphoric acid is then precipitated as

ammonium magnesium phosphate, and weighed as magnesium pyrophosphate. These methods yield equally trustworthy results. The quantity of phosphoric oxide found is multiplied by 11.36 to give lecithin. In the case of preparations which have been kept for a long time, or which have been maintained at a high temperature during manufacture, the above-mentioned method of extraction will not suffice to obtain all the lecithin in solution, and the alcohol extraction must be prolonged until the substance ceases to yield alcohol-soluble phosphorus compounds. W. P. S.

**Detection of Preservatives in Fats** (Butter, Margarine, Lard). E. VOLLMER (*Chem. Zeit.*, 1913, 37, 312).—Fifty grams of the fat are shaken with 100 c.c. of boiling water, two drops of 15% sodium hydroxide solution, and about 10 grams of solid paraffin. The mixture is then cooled, the aqueous layer is separated, and filtered. A portion of the filtrate is used for the detection of formaldehyde and sulphurous acid, the usual tests being employed. The remainder of the filtrate is now boiled after the addition of aluminium hydroxide, then cooled, and filtered. Separate portions of this filtrate are tested for the presence of salicylic acid, benzoic acid, fluorides, boric acid, and chlorates. W. P. S.

**Estimation of Coumarin in *Melilotus vulgaris* and *Officinalis*.** ERNST OBERMAYER (*Zeitsch. anal. Chem.*, 1913, 172—191).—Ten grams of the air-dried ground sample are extracted with ether in an extraction apparatus, and the ether is then evaporated in a 500 c.c. flask. The residue is submitted to distillation after introducing 300 c.c. of calcium chloride solution (1 kilo. in 3 litres) until the mass shows signs of solidifying. The heat should be regulated so that the operation lasts fully an hour.

The distillate is diluted to a definite mark, and then filtered. An aliquot part is taken for the estimation of the coumarin by titration with permanganate.

The neutral solution is mixed with zinc sulphate solution, then with standard permanganate, and boiled on an asbestos plate for ten minutes. When cold, the solution is passed through an asbestos filter, and the precipitate washed with water. The excess of permanganate is then found by titrating in the usual manner with oxalic acid, etc.

The titre of the permanganate is best verified by a check experiment with pure coumarin. L. DE K.

**Miscibility Curves for the Estimation of Dissolved Substances: Camphorated Alcohol.** HENRI ROSSET (*Ann. Chim. anal.*, 1913, 18, 49—56).—When a camphorated alcohol of unknown strength has to be tested for content in camphor and alcoholic strength, two experiments are made, one with nitrobenzene and another with essence of turpentine. Nitrobenzene is very sensitive to alcoholic strength; turpentine very sensitive to amount of camphor. The critical temperature of mixing is determined with the usual precautions in the apparatus of Louise, and by consulting



the curves in the original paper the strength of the sample may be readily ascertained. L. DE K.

**Reactions of the Digitalis Glucosides. Digitonin.** C. REICHMANN (*Pharm. Zentr.-h.*, 1913, 54, 217—221).—The following three reactions may be employed for the identification of digitonin. Small quantities of ammonium vanadate, sodium tungstate, and potassium iodate are placed on separate microscope slides, a small quantity of digitonin is added to each, together with a drop of glacial acetic acid, and the mixtures are allowed to dry. The slide containing the vanadate exhibits a green colour after a few hours, but this change is not due to the presence of the glucoside; the other mixtures do not change in colour. Concentrated sulphuric acid is now added to the mixtures; a dark green coloration is obtained with the vanadate mixture, and, after moisture has been absorbed from the atmosphere, a faint violet coloration develops. The iodate mixture is coloured violet-black, and iodine is liberated. The tungstate mixture remains unaltered; even when the temperature is raised, the salt is not reduced, but the mixture becomes green or greenish-black in colour, changes which are due to the action of sulphuric acid on the glucoside. Another characteristic reaction consists in evaporating a drop of cobalt nitrate solution by the aid of a gentle heat until a deep blue-coloured residue is obtained; a small quantity of digitonin and a drop of glacial acetic acid are then added, and the mixture is exposed to the atmosphere for about thirty hours, when a mass of red crystals is obtained. In the case of digitoxin, this test yields a moist green residue, but no crystals form. Reactions of digitonin with several other reagents are described.

W. P. S.

**Detection of Saponin.** LEOPOLD ROSENTHALER (*Zeitsch. Naturforsch.*, 1913, 25, 151—158).—When saponin is hydrolysed with dilute acids an intermediate product is obtained, in which the sapogenin is still combined with a quantity of sugar; this product, termed prosapogenin, yields an orange-red coloration with concentrated sulphuric acid, the colour changing gradually to red, and then to violet. When shaken with an alkali solution, prosapogenin yields a persistent froth. The liquid under examination is treated with 2.5% of hydrochloric acid, filtered if necessary, and then heated on a boiling water-bath until the mixture ceases to froth when shaken. The mixture is now cooled slightly, shaken with ethyl acetate, the latter then separated, washed with water, and evaporated to dryness. Should the ethyl acetate solution be dark in colour, it may be treated with animal charcoal before evaporation. The residue is then tested with sulphuric acid and with alkali solution as described. In the case of beer, it is necessary to heat the liquid with its own volume of 95% alcohol until a flocculent precipitate separates; this is removed by filtration, and the filtrate then hydrolysed and tested; or the beer may be evaporated and the residue extracted with 70% alcohol. Methods which depend on the hemo-

lytic action of saponin (A., 1912, ii, 819) are not always trustworthy, owing to the fact that certain saponins are devoid of this property.

W. P. S.

[Detection of] Antipyrine in Toxicological Analysis. G. Druce Lander and H. W. Wister (*Analyst*, 1913, 38, 97-98).—Antipyrine may be isolated from viscera, etc., by means of the Stas Otto process, the best final extraction medium being chloroform in the presence of ammonia.

The residue is then treated with 5 c.c. of Steensma's reagent and evaporated to dryness, when a beautiful rose-red colour is developed. It must be remarked that amyl alcohol, and also undenatured spirit, should be entirely absent, as they also yield a faint pink colour.

From urine, the antipyrine may be also isolated by simply shaking with chloroform, preferentially in the presence of ammonia.

Steensma's reagent is prepared by dissolving 1 gram of *p*-dimethylaminobenzaldehyde in 100 c.c. of a solution of 5 c.c. of 25% hydrochloric acid in 100 c.c. of absolute alcohol.

L. DE K.

Estimation of Morphine in Opium and its Preparations. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1913, [vii], 7, 162-163).—Seven and a-half grams of opium, dried at 60°, are mixed with 3 grams of finely powdered lime and 30 c.c. of water to form a homogeneous fluid, which is placed in a 125 c.c. flask, using 45 c.c. of water in several portions to wash the mortar and pestle used in making the mixture. After remaining two hours with occasional agitation, the mixture is filtered, and 52 c.c. of the filtrate (=5 grams of opium) placed in a 110-120 c.c. flask with 5 c.c. of acetone and 1 gram of ammonium chloride. After the latter has dissolved, the liquid is set aside for twenty-four hours, and the morphine which has then crystallised out is separated by filtration and washed first with water and then with acetone, both solvents having been first saturated with morphine.

In the case of opium extract, 3 grams are dissolved in 75 grams of water and mixed with 3 grams of lime. After two hours 65 grams of the filtrate (=2.5 grams of extract) are treated as described above. For laudanum (tincture of opium) 75 grams are evaporated to dryness at 100°, and the residue dissolved as far as possible in 75 c.c. of water, mixed with 3 grams of lime, and after two hours 52 c.c. (=50 grams of laudanum) are treated as described above.

T. A. H.

Estimation of Tyrosine in Proteins. EMIL AEDERHOLDEN and DIONYS FREUS (*Zeitsch. physiol. Chem.*, 1913, 83, 468-473).—See this vol., i, 409.

Nephelometry in the Study of Proteases. II. PHILIP A. KOBER (*J. Amer. Chem. Soc.*, 1913, 35, 290-292).—In an earlier paper (this vol., ii, 260) a method has been described for studying proteases and nucleases by precipitating the substrate as a suspension by means of a suitable reagent, and estimating the amount of

suspended matter with the nephelometer. It is now shown that the nephelometer can be used for investigating the digestion of casein when a 3% solution of sulphosalicylic acid is used as precipitant. This reagent does not precipitate amino-acids, peptides, peptones, or urinary constituents under the conditions observed in the experiments. The nephelometric constant ( $k$ ) for casein with this precipitant is 0.20.  
E. G.

**Arnold's Nitroprusside Reaction in Urine.** VINZENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1913, 83, 304—314. Compare A., 1907, ii, 115).—The violet coloration formed when a drop of 4% sodium nitroprusside solution, followed by alkali, is added to urine is produced, not only after taking meat or beef tea, but also, although relatively faintly, after taking pure carbohydrate or protein foods. The intensity of the reaction increases when the foods are taken in a prepared form so as to increase their digestibility. Beef tea causes the most marked reaction, which must accordingly be due to stimulating substances present among the substances in meat, to which it owes its flavour. The better flavoured the meat, the more intense is the violet reaction, which is entirely dependent on the intensity of the stimulus received. In cases of illness the reaction is entirely absent, but returns again during convalescence.

The chemical changes in the living cell receive a marked stimulus from the exciting substances in foods, particularly in meat. In a case of diabetes, when sufficient beef tea was administered with bread, so that a marked violet reaction in the urine was prolonged for two hours, no sugar was excreted. So long as the stimulus lasted the organs were able to utilise the sugar in the body.

The violet nitroprusside reaction is not confused with Weyl's creatinine reaction if only a single drop is added at first, and after waiting a few minutes when the violet colour has disappeared, more nitroprusside is added.  
E. F. A.

**Estimation of Colloids in Effluents.** PAUL ROHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 45—46).—A method of estimating the colloidal substances in factory effluents is described, which depends on the adsorption of dyes by the coagulated colloids. To 50 or 100 c.c. of the effluent, 1 c.c. of a 1% solution of aniline-blue is added, and the liquid evaporated to syrupy consistency on the water-bath. The coloured residue is then extracted with hot water, and after filtration the amount of unadsorbed aniline-blue is estimated colorimetrically.  
H. M. D.

**A Rapid Method of Determining the Quality of Drinking Waters.** B. GALLI-VALERIO and M. BORNAND (*Centr. Bakt. Paras.*, 1913, ii, 36, 567—573).—The use of Oldekop's neutral-red agar is recommended for the detection of contamination of the water by urea bacteria and especially *Bact. coli*. This is indicated by the appearance of fluorescence and the production of a canary-yellow colour when small quantities of the water to be tested are carried into slope tubes of the medium.  
H. B. II.

## General and Physical Chemistry.

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**Refractive Index of Substances at their Critical Temperatures.** EDMOND VAN AUBEL (*Physikal. Zeitsch.*, 1913, 14, 302—303).—According to Smith (A., 1912, ii, 1013), the calculated refractive index of a large number of substances is equal to 1.126 at the critical temperature. The author finds that the calculated values for aniline, carbon disulphide, and water are 1.164, 1.189, and 1.102 respectively. The divergent values obtained for the last two substances indicate that anomalous refraction at the critical point is not confined to aromatic substances or halogen compounds. The calculated value for ethyl ether is 1.121, which agrees with the result obtained experimentally by Galitzin and Wilip (A., 1900, ii, 461).  
H. M. D.

**Refraction and Dispersion of Gaseous Compounds and the Cause of the Divergence from Additive Relations.** CLIVE CUTHBERTSON (*Phil. Mag.*, 1913, [vi], 25, 592—604).—The deviations from the additive rule which are exhibited by gaseous compounds have been submitted to examination.

In the case of hydrogen chloride, bromide, iodide and sulphide, and sulphur dioxide, the refractivity of the compound is less than the sum of the refractivities of its constituents, whilst the dispersive power of the compound lies between those of the constituents.

On the other hand, the refractivity of nitrous oxide, nitric oxide, ammonia, and ozone is greater than the sum of the refractivities of the constituents, and the dispersivity is greater than that of either of the constituents.

In connexion with these relationships, it is pointed out that the spectra of chlorine, bromine, iodine, and sulphur, which occur in the first group, show strong absorption bands in the violet and ultra-violet regions which disappear in the compound; whereas nitrous oxide, nitric oxide, and ozone show absorption bands in the ultra-violet which are not present in the spectra of the elements.

In explanation of these facts, it is suggested that the refractivity of a gaseous element (excluding those which consist of monatomic molecules) or compound consists of two parts, which are distinguished as atomic and interatomic. The atomic refractivity is due to vibrations which are governed by forces resident in the atom, and may be assumed to remain nearly constant. The refractivity due to this mode of vibration is roughly 80 to 90% of the total refractivity measured in the visible region of the spectrum. The absorption connected with it is that which lies in the Schumann region. The interatomic refractivity is the result of the existence of free periods in the visible or neighbouring portions of the spectrum, and is due to forces which have their seat in more than one atom of the molecule. The absorption connected with these vibrations is that observed in the spectrum of these regions. The

interatomic refractivity of an atom varies according to the atom with which it is combined and with the nature of the linking

The changes in refraction, dispersion, and absorption, which occur when two elements combine together, are due to the disappearance of the interatomic refractivity and the appearance of new interatomic frequencies.

The relations existing between the compounds examined and the constituent elements are shown to be in accord with this hypothesis.  
H. M. D.

**Refraction and Dispersion of the Halogens, Halogen Acids, Ozone, Steam, Oxides of Nitrogen and Ammonia.** CLIVE CUTHBERTSON and (Mrs.) MAUDE CUTHBERTSON (*Phil. Trans.*, 1913, A, 213, 1—26).—It is well known that the refractivity of simple gaseous compounds is not in agreement with the additive law, and these measurements have been made in order to throw light on the cause of the anomalous behaviour. An account of the general results obtained, and of certain conclusions which have been drawn from them, has been published elsewhere (compare preceding abstract).

In most cases the refractivities have been measured with reference to the green mercury line ( $\lambda$  5461), and in order to correct for the deviations from the ideal gas laws, the refractivity ( $\mu - 1$ ) is reduced to the value which it would have if the density of the gas or vapour were equal to that of hydrogen (at  $0^\circ$  and 76 cm.) multiplied by the molecular weight of the substance referred to that of hydrogen. If the density thus defined is  $D$ , and the density of the substance at  $0^\circ$  and 76 cm. is  $d$ , then the corrected refractivity is represented by  $(\mu - 1)D/d$ .

Except where otherwise stated, the following values refer to  $\lambda$  5461: chlorine, 0.000784; bromine ( $\lambda$  6438), 0.001157; iodine ( $\lambda$  6438), 0.00210; hydrogen chloride, 0.000448; hydrogen bromide, 0.000615; hydrogen iodide, 0.0009258; water vapour, 0.000257; ozone, 0.00052; ammonia, 0.0003786; nitric oxide, 0.0002955; nitrous oxide, 0.0005100.

From the values of the refraction at other wave-lengths, the authors have also obtained numbers representing the dispersion of the various substances. In general, the dispersion can be represented quite satisfactorily by a formula of the Sellmeyer type.  
H. M. D.

**Some Liquid Mixtures Specially Suitable for the Observation of Christiansen's Phenomenon.** FERNAND LORMONT (*Compt. rend.*, 1913, 156, 772—774).—The author has found certain mixtures of two liquids which exhibit Christiansen's phenomenon (compare *Ann. Phys. Chem.*, 1884, 23, 298), and which are easier to prepare and work with than his mixtures of a liquid and a solid. One is prepared by the addition of 15 grams of ethyl acetate and 10 grams of water to 50 grams of a saturated aqueous solution of sodium chloride. This mixture is very sensitive to heat, that of the hand sufficing to modify the shadow colours. Another mixture is

prepared from a solution of 25 grams of sodium bromide in 35 grams of water by adding propyl alcohol drop by drop until the required effects are obtained. In repose the surface of separation of the liquids in these mixtures shows beautiful iridescences. W. G.

**A Modified Hufner Spectrophotometer.** RICHARD VON ZEYNEK (*Zeitsch. physiol. Chem.*, 1913, 84, 207—212).—Certain alterations in the Hufner spectrophotometer are described in detail and figured. They have the object of simplifying and facilitating the use of the instrument. E. F. A.

**Coloured Bunsen Flames.** ERNST BECKMANN and H. LINDNER (*Zeitsch. physikal. Chem.*, 1913, 82, 641—656).—A description is given of a modification of the apparatus of Beckmann and Waentig (A., 1910, ii, 1) for producing coloured Bunsen flames of constant intensity. The chief improvement in the apparatus lies in the method by which a constant supply of the salt solution is supplied to the rotating disk. This is achieved by allowing the liquid to flow through a jet 1.9 mm. diameter from a reservoir of constant level. The intensity of light measurements of sodium chloride flames produced by means of this apparatus were made by means of a König-Martens Grünbaum photometer. It is shown that flames of very constant intensity can be obtained in this way, and that the addition of other salts does not affect the intensity of the sodium flame as measured by the *D*-line. It is also shown that the distance between the vessel, in which the spray is produced, and the burner has an influence on the intensity of the flame. Various sodium salts were used in the experiments, and it was shown that the salts which contain oxygen give a somewhat more intense flame than the others. The intensity of the sodium flame is proportional to the square root of the concentration of the solution used (compare Arrhenius, A., 1891, 515; Gouy, *Ann. Chim. Phys.*, 1879, [v], 18, 5). Unsuccessful attempts were made to produce a constant potassium flame. In general it is shown that the electrical conductivity of sodium flames is increased by the addition of lithium salts. The addition of magnesium and calcium salts produces irregularities in the conductivity which are due to the non-volatile nature of the oxides of these metals. When these salts have been added, the conduction is unipolar and very considerable, and points to the existence of electrons. Quantitative analysis shows that the composition of the salt solution is the same in the flame as it is before the formation of the spray. J. F. S.

**Doppler Effect of the Series Lines of Oxygen.** HEINRICH WILSAR (*Physikal. Zeitsch.*, 1913, 14, 308—310. Compare this vol. ii, 172).—Polemical against Stark (this vol. ii, 172). In support of the author's statement that the series lines of oxygen do not show the Doppler effect, curves are drawn which show the distribution of the light intensity for both longitudinal and transverse exposures. Although these records afford no evidence of a Doppler effect, it is pointed out that this does not prove its absence. If the effect

does occur in the case of the series lines, it is, however, quite certain that the intensity of the displaced line is very small in comparison with that of the stationary line. H. M. D.

**Spectroscopic Study of the Electric Brush Discharge in Water and Salt Solutions.** HAROLD SMITH (*Phil. Mag.*, 1913, [vi], 25, 461—475).—The character of the brush and capillary discharge in water and aqueous solutions of lithium, sodium, potassium, and calcium salts has been investigated. The brush discharge was obtained by passing the current from a large induction coil between a platinum plate and an electrode constructed by sealing a platinum wire into a glass tube, and filing off the protruding end of the wire quite flush with the glass. In order to obtain the capillary form of discharge, this electrode was replaced by a quartz tube terminating below in a fine capillary, the actual electrode consisting of a platinum wire or plate supported in the upper wider portion of the quartz tube.

Under these conditions of discharge, the author has found the series and secondary spectrum of hydrogen, the series and elementary-line spectrum of oxygen, the spark lines of platinum, and also the spectra of the metals contained in the dissolved salts.

The series spectrum of hydrogen increases in intensity with increase in the current density, whilst the secondary spectrum is relatively less intense at higher densities. In the case of oxygen, the series spectrum is only observed at the higher current densities, whereas the elementary-line spectrum only appears with the feeble discharges.

The lines of the metal of the dissolved salt, which are observed in the brush discharge, appear to vary in relative intensity with the salt used and also with the current. In weak solutions these lines are destroyed when strong condensed discharges are passed between the electrodes. H. M. D.

**The Spectrum of the Univalent and of the Bivalent Helium Ion in the Canal Rays.** JOHANNES STARK, A. FISCHER, and H. KIRSCHBAUM (*Ann. Physik*, 1913, [iv], 40, 499—541).—From electromagnetic and spectral observations on canal rays, Stark has previously drawn the conclusion (A., 1911, ii, 678) that the carriers of the series lines are positive ions. According to this view it may also be expected that ions of the same element, which carry different charges, will give rise to different spectra.

In order to obtain information in support of this theory, the authors have investigated the Doppler effect for the lines in the canal-ray spectrum of helium. In regard to the choice of helium as the element to be investigated, it is pointed out that Runge and Paschen (A., 1896, ii, 1) have already shown that the helium spectrum contains two distinct groups of line series which led these authors to suggest that helium consists of two different elements. It seemed possible that these two groups might be due to helium ions carrying one and two charges respectively.

The experiments consisted in the photometric determination of the

distribution of the light intensity along the wave-length scale for various helium lines, observations being made in pure helium and in helium admixed with oxygen or iodine vapour. In presence of these electro-negative gases, the intensity maximum corresponding with the displaced lines is very clearly developed, whereas in pure helium there is no sharp distinction between the intensity due to the displaced and the undisplaced line.

The observations lead to the conclusion that both singly and doubly charged positive ions are present in the helium canal rays; further, that the carriers corresponding with the principal and the two subsidiary series of doublets are the singly charged ions, whilst the principal and two subsidiary series of simple lines are due to carriers which consist of doubly charged positive ions. The relation between the numbers of the two kinds of carriers depends on the conditions of the discharge, namely, on the pressure of the gas, the magnitude of the cathode fall of potential, and the presence or absence of an electro-negative gas.

H. M. D.

**The Wave-lengths of the Rays of Krypton.** HENRI BUISSON and CHARLES FARRY (*Compt. rend.*, 1913, 156, 945-947).—The spectrum of krypton presents some very fine lines, and is therefore of great value, especially when the tube is cooled in liquid air, for the observance of interference phenomena of luminous waves. The authors have used it, comparing the two intense lines in the green and yellow with the red line of cadmium, using interferences produced by thicknesses of 2, 5, 15, 25, and 100 mm. This comparison of the orders of interference obtained with cadmium and krypton gives with great precision the wave-lengths of the krypton lines.

W. G.

**Measurements in the Magnesium Spectrum with Reference to the International Normals.** ANDREAS NACKEN (*Zeitsch. wiss. Photochem.*, 1913, 12, 54-64).—Accurate wave-length measurements have been made in the arc and spark spectra of magnesium between  $\lambda=2630$  and  $\lambda=5710$ . In general, the spark lines are found to be much less sharp than those furnished by the arc. The data are compared with those obtained by previous observers.

H. M. D.

**Systems of Series [Lines] in the Spectra of Zinc, Cadmium, and Mercury.** FRIEDRICH PASCHEN (*Ann. Physik*, 1913, [iv], 40, 602-605). Further arguments are put forward in support of the author's contention that certain lines in the spectra of zinc, cadmium, and mercury form members of series which have not been previously described (compare A., 1910, ii. 3; 1911, ii. 833).

H. M. D.

**Spectral Investigation of the Arc Light between Carbons at Low Pressures.** MICHELE LA ROSA (*Ann. Physik*, 1913, [iv], 40, 542-550). The changes in the arc light spectrum have been examined when the pressure of the surrounding gaseous atmosphere is reduced. As the pressure falls, the arc discharge approximates in its general characters to that form which is associated with the



passage of the current through ordinary discharge tubes. The transformation from the one form to the other is not accompanied by any sudden changes in the electrical factors, although the spectra obtained in the two conditions are appreciably different. The change in the spectrum with gradually falling pressure would seem to indicate that there are a number of distinct phases in the transition from the normal arc to the normal low pressure discharge

H. M. D.

**The Absorption of Light by Water Changed by the Presence of Strongly Hydrated Salts, as Shown by the Radiomicrometer. New Evidence for the Solvate Theory of Solution.** J. SAM GUY, E. J. SCHAEFFER, and HARRY C. JONES (*Physikal. Zeitsch.*, 1913, 14, 278—288; *Amer. Chem. J.*, 1913, 49, 265—286. Compare A., 1912, ii, 711).—The radiomicrometer described in the previous paper has been employed in the investigation of the absorption of radiant energy by aqueous solutions of salts. The wave-length interval covered in the observations extended from about  $\lambda = 700\mu$  to  $\lambda = 1400\mu$ .

When the radiomicrometer readings obtained with an aqueous solution of a certain thickness are compared with those of a water layer, the thickness of which is arranged so that it is equal to that which would be given by the water in the solution, it is found that the absorption of radiant energy by the solution is very frequently quite different from the absorption produced by an equivalent thickness of pure water. This is at any rate the case for solutions of strongly hydrated salts, such as calcium chloride, magnesium chloride, and aluminium sulphate. The data obtained in similar experiments with aqueous solutions of potassium chloride, ammonium chloride, and ammonium nitrate show, on the other hand, no appreciable difference between the absorbing powers of the solutions and the layers of pure water, which are of equivalent thickness.

It is supposed that the observations indicate that the water which enters into combination with the salts of the first group has a smaller capacity for absorbing the incident radiation than water which is in the free condition. The general results can therefore be interpreted quite satisfactorily in terms of the solvate theory.

Incidentally it has been found that the water absorption bands are displaced by the dissolved salt towards the region of greater wave-lengths, the extent of the displacement increasing with the concentration of the solution. This effect is obtained independently of the hydrate-forming capacity of the dissolved salt. H. M. D.

**The Absorption of the Ultra-violet by Ozone, and the Extremity of the Solar Spectrum.** CHARLES FABRY and HENRI BRISSON (*Compt. rend.*, 1913, 156, 782—785).—A determination of the variation of  $a$ , the constant of absorption for ozone, as defined by the equation  $I = I_0 \cdot 10^{-ad}$ , where  $I$  and  $I_0$  are the intensities of the light before and after absorption, and  $d$  the thickness in cm. of pure gaseous ozone,  $\lambda$  varying from 2300 to 3400. The maximum absorption takes place at  $\lambda 2550$ , is very high at this point, and

the absorption varies rapidly between  $\lambda$  2900 and 3300, the value of  $a$  being given by  $\log a = 17.58 - 0.00564 \lambda$ . From these results, combined with measurements made on the amount of sun's light transmitted by the atmosphere, the authors draw the conclusion that the ozone content of the atmosphere, if evenly distributed, would be equal to 0.6 c.c. per cub. metre of air.

W. G.

**Absorption of the Ultra-violet Rays by Acetone.** JEAN BÉLÉCKI and VICTOR HENRI (*Compt. rend.*, 1913, 156, 881—886).—By photometric measurements of the spectrographs obtained from a condensed iron-cadmium spark, the light passing through either an aqueous or an alcoholic solution of acetone or through pure acetone, in layers of varying thickness, the authors have determined the values of the molecular constant of absorption,  $\epsilon$ , in the formula  $I = I_0 e^{-\epsilon c l}$  for values of  $\lambda$  from 2144 to 3706. The results show that acetone, in solution or in the liquid state, possesses only one absorption band in the ultra-violet, the maximum being at  $\lambda$  2706 for alcoholic solutions, and at  $\lambda$  2618 for aqueous solutions, there being no indication of the second band mentioned by Gelbke (this vol., ii, 87). The absorption curve, between  $\lambda$  2405 and 2981, can be very exactly represented by the Ketteler-Helmholtz-Reiff-Drude formula,  $\epsilon = a\lambda^2 / \{(\lambda^2 - \lambda_m^2)^2 + g^2\lambda^2\}$ , where  $a$ ,  $g^2$ , and  $\lambda_m$  are three constants. From calculation it is found that about one molecule in forty takes part in the absorption of the ultra-violet light by acetone.

W. G.

**Applications of the Electron Conception of Positive and Negative Valencies. V. Absorption Spectra and Dynamic Formulæ of Chloro-, Bromo-, and Iodo-benzene.** HARRY S. PRY (*Zeitsch. physikal. Chem.*, 1913, 82, 665—687. Compare A., 1911, i, 431; 1912, ii, 713).—The theory described in the previous papers is applied to the halogen mono-substitution products of benzene. Chloro- and bromo-benzene, since they both exhibit seven absorption bands, are stated to possess the same dynamic formulæ as benzene itself. The absorption spectra of these substances are discussed on the basis of the theory, and it is shown from the measurements of the absorption spectra (Baly, T., 1911, 99, 856; Purvis, T., 1911, 99, 811) that the frequencies of the absorption bands of a substance can be represented as a linear function of a series of even numbers, which represent the number of absorption changes ("contraplex-diplex" changes). The non-absorption of iodobenzene both in alcoholic solution and in thin layers of the pure substance is explained, in opposition to Purvis (T., 1912, 101, 1821), as due to the unsaturated nature of the iodine, which prevents the nucleus taking up the centric form.

J. F. S.

**Ultra-violet Absorption Bands of the Reciprocal Linking of Carbon Atoms.** JOHANNES STARK, WALTER STEURING, CORNELIS J. ENKLAAR, and PETER LUTF (*Jahrb. Radioaktiv. Elektronik*, 1913, 10, 153—174).—A large number of hydrocarbons have been examined with reference to their behaviour towards ultra-violet rays of short

wave-length. By means of a fluorspar spectrograph, it has been possible to obtain satisfactory photographic records of the absorption spectrum as far as  $\lambda=185\mu$ , and in this way the region covered by previous investigators has been considerably extended. The hydrocarbons were examined in the form of vapour, the rays being caused to pass through a layer of constant thickness, whilst the pressure was reduced in a series of steps in order to obtain the spectrum for different concentrations. Curves are plotted from the photographs, the pressure of the vapour and the wave-length being adopted as the co-ordinates.

The experimental observations are interpreted in accordance with the view that the absorption of ultra-violet light is a specific property of the carbon atom. The seat of the absorption is supposed to be the valency electron, and the position of the absorption band is further supposed to depend on the linking with which the valency electron in question is associated.

The accumulated data indicate that the linkings  $C-H$  and  $C-C$  do not give rise to an absorption band at wave-lengths greater than  $\lambda 185$ ; bands are found in this region, however, in the case of the linkings  $C=C$  and  $C\equiv C$ . Hydrocarbons which contain asymmetric double or triple linkings give rise to two broad bands, and it may therefore be supposed that the four or six valencies associated with the  $C=C$  and  $C\equiv C$  linkings respectively are approximately equivalent as regards their ultra-violet absorption, and the bands may therefore be regarded as peculiar to the linking as a whole.

The presence of two or more  $C=C$  or  $C\equiv C$  linkings in the molecule of a substance has an appreciable influence on the position as well as on the intensity of the absorption, and the nature of these effects is indicated by the curves obtained for different classes of hydrocarbons.

*The C-C Linking* (Hexane, cyclohexane, Camphane).—The data for these hydrocarbons indicate that the  $C-C$  linking, whether in an acyclic or a cyclic compound, does not give rise to selective absorption above  $\lambda 185$ . Although the observations do not show a fully developed band, it would appear that ring formation causes a shift towards the long-waved region.

*The Single Non-cyclic C=C Linking* (isobutylene,  $\beta$ -Methyl- $\Delta^3$ -butylene, Hexylene, Octylene).—Two absorption bands are evident, the first and less intense band having its head in the region  $\lambda 230-\lambda 205$ , and the second at about  $\lambda 180$ . The heads appear to shift according to the nature of the groups associated with the carbon atoms.

*Two Isolated Non-cyclic C=C Linkings* (Diallyl, Geraniolene).—Two bands are also found in this case, the heads being situated at about the same positions as those found for the single linking. The intensity is, however, very much greater than that associated with the single linking.

*Two Conjugated Non-cyclic C=C Linkings of similar type* ( $\beta$ -Methylbutadiene,  $\beta$ -Dimethylbutadiene,  $\delta$ -Methyl- $\Delta^2$ -pentadiene,  $\Delta^2$ -Hexadiene).—Compared with the single  $C=C$  linking, the head of the first band is shifted to  $\lambda 255-\lambda 235$ , and that of the second to about  $\lambda 210$ . The shift in both cases is about 20 to 30  $\mu$ , and a

the same time the intensity of the bands, particularly that of the first, becomes very much greater.

*The Single C=C Linking* (Camphene, Bornylene,  $\alpha$ -Pinene).—The first band is not exhibited. On account of its small intensity, its appearance would probably require greater pressures than those employed in the observations. The head of the second band is at  $\lambda 201$ — $\lambda 198$ , that is to say, the band is shifted towards greater wave-lengths as a result of the polycyclic linking.

*Two or More Dissimilar C=C Linkings* (Limonene, Sylvestrene,  $\alpha$ - and  $\beta$ -Phellandrene, Dimethylfulvene).—In limonene and sylvestrene, the C=C linkings are isolated, and the head of the second band only is shown by the extinction curves. Its position is about  $\lambda 185$ . In the case of  $\alpha$ - and  $\beta$ -phellandrene, both bands are clearly developed. The heads of the bands of the  $\alpha$ -compound are at  $\lambda 258$  and  $\lambda 210$ , those of the  $\beta$ -compound at  $\lambda 228$  and  $\lambda 198$ . In both compounds the C=C linkings are conjugated. The shift resulting from the conjugation is much more marked in the case of  $\alpha$ -phellandrene, which contains the two linkings in the six-C ring, whilst the  $\beta$ -compound has one linking outside the ring. Compared with the curves for limonene and sylvestrene, those for the two phellandrenes show very clearly the effect of conjugation.

Dimethylfulvene, which contains three C=C linkings, exhibits three well-developed broad bands with the heads at  $\lambda 370$ ,  $\lambda 258$ , and  $\lambda 207$  respectively. The middle band is the most intense. It is supposed that  $\lambda 207$  belongs to the semicyclic C=C linking, the longer-waved band corresponding with this not having been developed at the pressures employed in the examination. The two other bands are attributed to the endo-cyclic linkings, displacement towards greater wave-lengths having occurred to a very large extent as a result of the double conjugation.

*The Symmetrical C=C Linking* (Ethylene).—Up to atmospheric pressure, ethylene shows only one band at about  $\lambda 195$ , and this is resolved into a series of narrow bands. It is therefore quite different in character from the short-waved bands attributed to the asymmetric C=C linkings in the hydrocarbons investigated above. Although only one band was found with ethylene, the authors consider that the longer-waved band would be found at higher pressures. Liquid ethylene was, in fact, found to absorb ultra-violet rays up to  $\lambda 235$ .

The above results show that the carbon valency associated with an asymmetric C=C linking, whether in a cyclic or an acyclic compound, gives rise to two broad bands in the ultra-violet region above  $\lambda 180$ . As compared with the position of the bands due to a single C=C linking, it appears that the bands are displaced towards greater wave-lengths, and at the same time intensified, if the C=C linking is endo- or semi-cyclic, or if the linking is conjugated with reference to a second C=C linking.

H. M. D.

Ultra violet Absorption Bands of the Reciprocal Linking of Carbon Atoms. II. Acetylene Linking. JOHANNES STARR and PETER LEE (*Jahrb. Radioaktiv. Elektronik*, 1913, 10, 175—178. Compare preceding abstract).—The influence of the acetylene

linking on ultra-violet absorption has been investigated in reference to dipropargyl and acetylene. The extinction curve for dipropargyl shows two well-developed bands, the first of which has its head at  $\lambda=245\mu$  and the second at  $\lambda=201\mu$ . The second band is much deeper than the first. It is supposed that the two bands correspond with the pair which have been found to be characteristic of the asymmetric ethylene linking. The absorption curve for acetylene exhibits a large number of narrow bands in the region of the second dipropargyl band, the intensity of which increases as the wave-length diminishes. As in the case of ethylene, these narrow bands are only obtained at comparatively high pressures, and it is probably on this account that the less intense absorption band, which would be expected at greater wave-lengths, has not been actually observed.

H. M. D.

**Ultra-violet Absorption Bands of the Reciprocal Linking of Carbon Atoms. III. Benzene Linking.** JOHANNES STARK and P. LEVY (*Jahrb. Radioaktiv. Elektronik*, 1913, 10, 179-188, Compare preceding abstract).—In addition to the narrow group of bands between  $\lambda=270$  and  $230\mu$ , the absorption spectrum of benzene shows a much more intense group of similar bands in the region  $\lambda=210$  to  $\lambda=190\mu$ . Naphthalene behaves in the same way, a group of narrow intense bands being found in the region  $\lambda=250$  to  $\lambda=190\mu$  in addition to the less intense group situated between  $\lambda=310$  and  $\lambda=230\mu$ . Both the naphthalene bands are displaced towards the direction of greater wave-lengths relatively to the corresponding benzene bands.

The absorption spectra of cyclohexene and  $\Delta^{1:3}$ -cyclohexadiene, on the other hand, exhibit unresolved broad bands differing completely from the groups of narrow bands shown by benzene and naphthalene. The less intense band of cyclohexene is situated in the neighbourhood of  $\lambda=220\mu$ , and the head of the second band lies at about  $\lambda=190\mu$ . The heads of the corresponding bands of  $\Delta^{1:3}$ -cyclohexadiene are at  $\lambda=260$  and  $\lambda=213\mu$  respectively. As a consequence of the conjugation of the ethylene linkings in this substance, the bands are displaced towards the visible region, and the intensity of the absorption, particularly that of the first band, is greatly increased.

From the totally different character of the benzene bands as compared with those of cyclohexene and  $\Delta^{1:3}$ -cyclohexadiene, the conclusion is drawn that the benzene ring contains no normal ethylene linkings. The relationships between the carbon atoms are of a specific kind, and this necessitates the assumption of a benzene linking.

Reference is made to the fact that the observed molecular refractivity of benzene agrees with that calculated on the assumption that benzene contains three normal linkings. This agreement does not, however, justify the conclusion that three such linkings are present. According to the author, the ultra-violet absorption of benzene would seem to show that the agreement is accidental and due to the circumstance that the refractivities of the actual linkings

are mutually affected by their close approximation (as in the case of conjugated ethylene linkings), and that the modified refractivity is practically equal to the refractivity of a normal ethylene linking.

H. M. D.

**Absorption of Ethylbenzene in the Ultra-violet.** GRONG WEINER (*Zeitsch. wiss. Photochem.*, 1913, 12, 33—53).—The absorption spectrum of ethylbenzene has been examined over the interval  $\lambda = 2300$  to  $\lambda = 2750$ , observations being made on the vapour at temperatures between  $20^\circ$  and  $80^\circ$ , and on ethyl-alcoholic solutions containing from 0.02 to 50% of ethylbenzene. In both cases, the spectrum consists of a series of bands which are shaded off towards the red end of the spectrum. With rise of temperature, the vapour bands broaden out towards the red end, but the short-waved edges of the bands are unaltered in position by either change of temperature or of the thickness of the vapour column. In the case of the solution spectrum, on the other hand, it is found that the bands are displaced towards the red as the concentration is increased.

On comparing the ethylbenzene spectrum with that of toluene, it is seen that the two are identical except for the fact that the former is displaced towards the ultra violet to the extent of  $0.7\mu$ . The wave-length measurements in the vapour spectrum indicate that this consists of ten series of bands, which can be represented by means of Deslandres' formula. In the solution spectra the undivided bands become more or less merged together, but even in this case it is found that the wave-length data indicate the existence of a definite series.

H. M. D.

**Absorption Spectra and Constitution of Benzene Derivatives. III. Phenols and Methoxy- Aldehydo- and Nitro-phenols in Alkaline Solutions.** NICOLAI A. VALIASCHKO (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 199—239. Compare A., 1910, ii, 1015, and 1911, ii, 2).—The author has investigated the influence of sodium ethoxide on the absorption spectra in alcoholic solution of phenol (also in water with sodium hydroxide), *o*-, *m*-, and *p*-methoxy-phenols, *o*-, *m*-, and *p*-hydroxybenzaldehydes, and *o*-, *m*-, and *p*-nitro-phenols.

With phenol and the methoxyphenols, the spectrometric results show that replacement of the hydroxylic hydrogen by sodium is not accompanied by change in the structure or condition of the molecules, although the absorption spectra undergo intensification and also displacement towards the red portion of the spectrum.

The molecules of the isomeric hydroxybenzaldehydes and nitro-phenols exist as salts in the same condition as in the free state, and retain their different peculiarities. In neutral solutions the ortho isomerides form equilibrated systems of two forms of molecules,  $\alpha \rightleftharpoons \phi$ , the former being intense, and the latter weaker modifications (*loc. cit.*); by formation of the corresponding sodium phenoxides, the  $\alpha$  form is strengthened considerably, and the  $\phi$ -form slightly. *Meta* isomerides also form equilibrated mixtures, the

$\alpha$ -form being here less, and the  $\phi$ -form more, developed than with the ortho-compounds; replacement of the hydroxylic hydrogen by sodium intensifies both forms, the equilibrium being displaced towards the  $\phi$ -modification. In neutral solution the para-isomerides exist in the phenolic condition, and when sodium replaces the hydroxylic hydrogen the  $\phi$ -form is considerably intensified, and there appears a weak  $\alpha$ -form, which may indeed be present, although ill-defined, in neutral solutions. The intensification which thus takes place in the form already existing in solution finds expression in increase of the region of absorption and its displacement towards the red end of the spectrum.

The bearing on these results of the views expressed by Baly, Tuck, and Marsden (T., 1910, 97, 584) and by Hantzsch and Voigt (A., 1912, i, 151) is discussed.

T. H. P.

**Colour and Optical Activity.** ERNESTO LONGOBARDI (*Anal. Soc. Quim. Argentina*, 1913, 1, 58—66).—Attempts to resolve  $\alpha$ -tyrosine and alkali-blue-6B by selective fixation on wool and silk gave negative results.

G. D. L.

**Processes Operative in Solutions. XXVI. Disturbance of the Equilibrium in Solutions of Lævulose by Salts and by Non-Electrolytes.** E. E. WALKER (*Proc. Roy. Soc.*, 1913, A, 88, 246—252).—If a solution of lævulose is heated and then quickly cooled to 25°, it is found that the optical rotatory power is altered, but that it gradually returns to the initial value in accordance with the formula for a unimolecular reaction. The same thing is observed if the lævulose solution is cooled and then rapidly warmed to 25°. This seems to show that the proportions in which the two isodynamic forms are present in the equilibrium condition vary considerably with the temperature. Evidence has been obtained that the change in rotatory power produced by the addition of ethyl alcohol is due to the same cause, this change being approximately proportional to the amount of alcohol which is added to a fixed quantity of water.

On the assumption that this is the cause of the change in the rotatory power, the author has investigated the influence of certain salts and non-electrolytes on the rotatory power of an aqueous solution of lævulose. The results indicate that methyl alcohol and its homologues, methylal and paracetaldehyde, favour the formation of  $\alpha$ -lævulose, whereas phenol, sucrose, lævulose itself, and sodium and potassium chloride appear to have the opposite effect. In the case of the salts, it is suggested that the observed change in rotation may be in part due to the formation of compounds with the lævulose.

H. M. D.

**Magnetic Rotatory Polarisation of Liquid Nitrogen and Oxygen.** J. CHAETTER (*Compt. rend.*, 1913, 156, 1008—1010).—A study of the magnetic rotatory power and the rotatory dispersion of liquid nitrogen and oxygen. The magnetic rotation is proportional to the intensity of the field and the thickness traversed.

At 18° the magnetic rotatory power is positive in both cases, and the values found are: for nitrogen,  $\rho_D = 0.00415$ ; for oxygen,  $\rho_D = 0.00782$ ; and for carbon disulphide,  $\rho_D = 0.012$ . The magnetic rotatory dispersion of nitrogen varies inversely as the square of the wave-length, and is very close to that of methyl chloride. Oxygen has a feeble rotatory dispersion, and does not obey the law of inverse squares, the values found being less than those calculated. The results obtained for the magnetic rotatory dispersion are analogous to those obtained by Becquerel for gaseous nitrogen and oxygen (compare *J. Physique*, 1880, 9, 265). W. G.

**Energy Absorbed in Photochemical Reactions.** VICTOR HENRI and RENÉ WURMSER (*Compt. rend.*, 1913, 156, 1012—1015).—The authors have measured the amount of energy necessary for the photochemical decomposition of a molecule in the case of hydrogen peroxide and acetone, and also the minimum of energy capable of provoking a luminous sensation in the eye, and in every case obtain values inferior to the "quantum of energy" according to Einstein. They suggest that the energy necessary for the decomposition of a molecule might serve as a measure of the degree of stability of the substance. W. G.

**The Dissociation of Gaseous Compounds by Light; Gaseous Hydrogen Compounds of the Chlorine and Oxygen Groups.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 156, 889—892. Compare A., 1910, ii, 606).—A study of the stability of the hydrogen compounds with the members of these two groups of elements towards light of different wavelength. As in the case of decomposition by heat, it holds good that, in the same family of elements, the stability of the hydrogen compounds with respect to light decreases as the atomic weight increases. Substances which are only dissociated at high temperatures are similarly only affected by the very rapid vibrations of the extreme ultra-violet light. Hydrogen chloride requires ultra-violet light ( $\lambda < 0.2\mu$ ) for decomposition, which even then is slow, whilst under similar conditions hydrogen bromide is rapidly and completely decomposed. Hydrogen iodide is decomposed by blue and violet light. A similar relationship is found in the case of water vapour, hydrogen sulphide, selenide, and telluride. W. G.

**The Production of Light by Chemical Action.** J. HERBERT VINCENT and J. MARLEY (*Chem. News*, 1913, 107, 138).—The authors cannot find any effect on a photographic plate of the following reactions: Action of sulphuric acid on zinc; action of hydrochloric acid on sodium metasilicate; action of nitric acid on lead; hardening of plaster-of-Paris; electrolysis of water with platinum electrodes. These observations contradict those of Maruschek and Neming (A., 1912, ii, 116), and it is difficult to account for the positive effects obtained by them. Experiments showed that the heat produced by chemical action does not give the effect. No experimental details are given. T. S. P.



**Decomposition of Lactic Acid under the Influence of Sunlight.** DOMENICO GANASSINI (*Chem. Zentr.*, 1913, i, 387; from *Giorn. Farm. Chim.*, 1912, 61, 540—547).—The author upholds his statement that lactic acid decomposes into acetaldehyde, pyruvic acid, and carbon dioxide under the influence of sunlight and air (*Giorn. Pharm. Chim.*, 1910, 48, 785), and explains Neuberg's contradictory conclusion (*A.*, 1912, ii, 314) by the fact that the latter worker used sterilised solutions in hermetically sealed quartz vessels.  
J. C. W.

**Quantitative Investigation of the Photochemical Transformation of *o*-Nitrobenzaldehyde into *o*-Nitrosobenzonic Acid.** FRITZ WEIGERT and LUDWIG KUMMERER (*Ber.*, 1913, 46, 1207—1218).—The transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzonic acid under the influence of light (compare Ciamician and Silber, *A.*, 1901, i, 390) is independent of air; it is a simple case of isomeric change, and may therefore be taken as a typical, specific light reaction. In order to study the process quantitatively, acetone had to be chosen as solvent, since the acid would be esterified by alcohol, and is only sparingly soluble in other media. A simple titration of the acid was found to be untrustworthy even with fluorescein or Hewitt's azo-dyes (*A.*, 1908, ii, 269) as indicators. Samples of the solution were therefore diluted with water and submitted to conductivity measurements, a curve having been obtained empirically. The solutions were exposed in glass troughs to the rays from a quartz mercury lamp (compare Weigert, *A.*, 1909, i, 219), being protected from heat rays by a tank of running water, and, as occasion required, filters of nitrosodimethylaniline in 0.001% solution and quinine sulphate in 0.05% solution were interposed to cut off the violet and blue and ultra-violet light respectively. The light absorbed by the filters and by solutions of the two substances was photometrically determined by POHL and PRINGSHEIM.

Preliminary experiments showed that the same results were obtained under the same conditions, that it was unnecessary to stir the solutions, and that the amount of transformation was practically proportional to the time of illumination. In order to study the influence of the intensity of the light, the lamp was stopped down so as to make the source of light approximate to a point, and the solutions were placed at such distances that the intensities were in the ratio 4 : 2 : 1, and then illuminated for periods which varied as 1 : 2 : 4. It was found that slightly less transformation had occurred in the most remote vessel, thus showing that the Bunsen-Roscoe law, that the same quantity of light produces the same chemical effect, is not quite admissible.

In further experiments on the influence of the initial concentration of the solution, the light was filtered through the quinine sulphate or nitrosodimethylaniline solutions, when, after allowing for the amount of light absorbed by these filters, it was found that the sum of the quantities of *o*-nitrosobenzonic acid formed was practically equal to the amount produced, under otherwise similar conditions, by unfiltered light. In the case of ultra-violet light, the

effect is independent of the concentration, but for violet light the speed of transformation is, at first, proportional to the concentration. The order of the reaction therefore changes with the kind of light, so that no simple law can be deduced to express the quantitative course of the reaction. No proportion existed either between the speed of the reaction and the amount of light absorbed by the aldehyde, although they increased in the same direction. With mixed light, the chief work is done in dilute solutions by the ultra-violet rays, and in concentrated solutions by the violet.

Kailan (this vol., i, 51) has recently made similar experiments, but not with the same degree of refinement, and his results are criticised.

J. C. W.

**Physico-chemical Studies on Photographic Developers.** (Correction.) NIKOLAI SCHILOV and S. FEDOTOV (*Zeitsch. Elektrochem.*, 1912, 19, 268).—Reference is made to the paper by Leubner and Luther (A., 1912, i, 254), which confirms the conclusions of Schilov and Fedotov (A., 1912, i, 966). The authors correct printers' errors in the original paper (*loc. cit.*).

J. F. S.

**The Secondary Radiation Produced by  $\alpha$ -Rays.** B. BLANC (*Compt. rend.*, 1913, 156, 785—788).—The author has studied the secondary radiation from  $\alpha$ -rays by measuring the current produced in an ionisation chamber by the radiation from a metallic surface bombarded by  $\alpha$  rays. The results confirm the existence of a secondary radiation, easily absorbed, capable of ionising and carrying a negative charge, the velocity deduced for it being  $1.8 \times 10^9$  cm./sec.

W. G.

**Laws of Deflexion of  $\alpha$ -Particles through Large Angles.** HANS GEIGER and ERNEST MARSDEN (*Phil. Mag.*, 1913, [vi], 25, 604).—From Rutherford's theory of the constitution of the atom it has been deduced that the single scattering of  $\alpha$ -particles through large angles should occur according to a formula which has been made the subject of experimental test. (1) The number of  $\alpha$ -particles emerging at an angle  $\phi$  with the initial direction should vary as  $\text{cosec}^4 \phi/2$ . This was found to hold good for angles  $\phi$  between  $5^\circ$  and  $150^\circ$ , in which range the number of  $\alpha$ -particles varied from 250,000 to 1. (2) The number of  $\alpha$ -particles scattered in any definite direction should be proportional to the thickness of the scattering foil. For small thickness this was found to be the case. For larger thicknesses the decrease in the velocity of the  $\alpha$ -particle causes a rapid increase in the amount of scattering. (3) The scattering should vary approximately as the square of the atomic weight of the scattering material. This was found to be the case for materials of atomic weight between carbon and gold (Au, Pt, Sn, Ag, Cu, Al, C). (4) The amount of scattering varies approximately as the inverse fourth power of the velocity of the incident  $\alpha$ -rays. This was verified over a range such that the number of  $\alpha$ -particles scattered varied in the ratio of 1:10. (5) Quantitative measurements of the absolute fraction of  $\alpha$ -particles of radium-C

scattered showed that, for  $\phi = 45^\circ$  and a gold foil equivalent to 0.1 cm. of air ( $2.1 \times 10^{-6}$  cm. thick),  $3.7 \times 10^{-7}$  of the  $\alpha$ -particles were counted on a screen 1 mm.<sup>2</sup> area at a distance of 1 cm. from the foil. From this figure and the theoretical relation, it was deduced that the central charge of an atom consisted of a number of elementary charges equal to about one-half the number representing the atomic weight. Only single scattering is dealt with. Compound scattering, due to combination of a large number of deflections, in greater thicknesses of material is probably due, not only to the central charge of the atom, but to the electrons distributed through the volume of the atom. F. S.

**Helium in Thermal Springs and Earth Gases.** HERR, SIEVEKING and L. LAUTENSCHLAGER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 62—64).—Nitrogen was separated from the purified gases by means of a mixture of magnesium powder, sodium, and calcium oxide. The helium was separated from the rare gases by freezing out the latter in the usual way. The activity of the gases, etc., expressed in volts/hours, was determined with an Engler-Siebeking fontakoscope.

The results show that the stulm gases all show a higher percentage of helium than the water and sediment from the springs. The gases obtained directly from the springs contain considerably more helium than the stulm gases, since the latter communicate with the outside air.

There appears to be no numerical relation between the radioactivity and the content of radium. T. S. P.

**Excitation of  $\gamma$ -Rays by the  $\alpha$ -Rays of Ionium and Radium thorium.** JAMES CHADWICK and ALEXANDER S. RUSSELL (*Proc. Roy. Soc.*, 1913, A, 88, 217—229).—The source of  $\alpha$ -rays consisted of 1.2 grams of thorium oxide containing the ionium in equilibrium with 3.6 mg. of radium. It was purified from all other radioactive substances before use by repeated precipitation of the hydroxides with ammonia, and, lastly, in nearly neutral solution with *m*-nitrobenzoic acid in excess. A small activity, due to  $\beta$ - and  $\gamma$ -rays, remained constant for ten days after purification, and can only be due to the ionium. Only 10% was due to  $\beta$ -rays, and part of this at least may be due to products of thorium. The remainder was not deviated by a magnetic field of 1000 gauss, when the preparation was spread over an area of 15 cm.<sup>2</sup> at a distance of 9 cm. from the base of the electroscope. The conclusion was reached that it consists of a  $\gamma$ -radiation excited by the  $\alpha$ -rays of ionium in the material itself (Chadwick, this vol., ii, 91).

By measurements of the absorption in aluminium the radiation was analysed into three types, each exponentially absorbed. The first is completely absorbed, after passage through 9 cm. of air, by 0.003 cm. of aluminium, and the value of  $\mu/D$  was about 520 (cm.)<sup>-1</sup>. From the whole preparation, 1.2 grams, disposed as stated, it contributed 32% of the ionisation, but in the form of a very thin film the effect produced by it is large compared with the other types.

The second type of medium penetrating power had a value for  $\mu/D$   $9.4 \text{ (cm.)}^{-1}$ , and contributed 60% of the ionisation; whilst the third and most penetrating type had a value of  $\mu/D$   $0.17 \text{ (cm.)}^{-1}$ , and contributed only 8% of the ionisation, which corresponded with less than one division per minute. Correcting for the obliquity of the beam, the values of  $\mu/D$  are 400, 8.35, and  $0.15 \text{ (cm.)}^{-1}$ , and the relative energies of the beams, roughly evaluated, as 15 to 0.075 to 0.2. The second type of medium penetrating power corresponds with the characteristic X-radiation of thorium, and it is probable that the other two types correspond with still unknown X-radiations in different series.

Experiments with radiothorium showed that it also emitted a  $\gamma$ -radiation, which was too small and too quickly masked by the growth of products to be studied in detail.

F. S.

**Production of Fluorescent Röntgen Radiation.** WILLIAM H. BRAGG (*Phil. Mag.*, 1913, [vi], 25, 657—659).—A reply to J. Crosby Chapman (*ibid.*, 359), defending the hypothesis that the energy is conveyed from the primary X-ray to the homogeneous secondary X-ray by an intermediary cathode-ray, in which a preliminary account is given of work done in conjunction with PORTER. The molybdenum X-rays have been compared with the selenium X-rays in their action on ethyl bromide and on sulphur dioxide. Bromine, being intermediate in atomic weight between selenium and molybdenum, the molybdenum X-rays, but not the selenium X-rays, can excite the bromine X-rays. Various expected effects have been looked for, and in some cases found. The cathode ray produced by the molybdenum X-ray, for example, should show deficiency in penetrating and ionising power in ethyl bromide, since its energy is being otherwise utilised. The same considerations apply, also, to the two kinds of X-rays. Also, secondary bromine X-rays should result by molybdenum cathode rays, but this has not yet been established.

F. S.

**Ionisation Accompanying Flame Gases.** HENRI JACQUES FROUJEN (*Bull. Soc. chim. Belg.*, 1913, 27, 80—90. Compare A., 1910, ii, 381, 479).—In extension of previous work, it is now shown that ionisation persists in the gases resulting from the flame of a candle, even when these have been kept for a considerable time after the extinction of the flame. Details of the methods of collecting the gases and measuring the degree of ionisation are given. The following conclusions are drawn: Gases from a candle flame show a residual ionisation, even after some hours of repose in a glass vessel, which may be due to persistence of initial ionisation or to the formation of ions by a change in state of the gases. This ionisation can be detected by obtaining current-potential curves. Ohm's law is followed at first, but eventually the current increases less rapidly than the potential. The gases collected exhibit an excess of negative charges, and show only slight mobility.

T. A. H.

**Photo-electric Emission of Electrons by Calcium.** ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1913, 15, 111—122. Compare A., 1912, ii, 317, 618, and previous papers).—The photoelectric properties of calcium have been examined by a method similar to that used in previous experiments with the alkali metals, magnesium, and aluminium. Over the wave-length interval  $\lambda = 230$  to  $\lambda = 700\mu$ , the emission is of normal character, being independent of the orientation of the direction of vibration of the incident light with reference to the plane of incidence. The number of electrons emitted per unit quantity of absorbed light energy varies with the wave-length, a maximum effect being obtained at about  $\lambda = 365\mu$ . This maximum becomes more pronounced as the angle of incidence of the exciting light diminishes; in the case of grazing incidence the maximum disappears, and the emissive effect then increases continuously as the wave-length falls. The observed dependence of the photo-electric emission on the angle of incidence is just the reverse of that which was found in the case of the selective photo-electric effect of the alkali metals.

H. M. D.

**The Mechanism of Disintegration of Radioactive Substances.** F. BUTAVAND (*Le Radium*, 1913, 10, 75—80).—This purely theoretical and speculative paper is based on an analogy between the distance of the planets in the solar system and the type of atom postulated for radium and the radio-elements.

F. S.

**Preparation of Solid Therapeutically Active Compounds of Radium.** EMANUEL MERCK and WILHELM EICHHOLZ (D.R.P. 256686).—It has been previously shown by Wassermann (*Deut. med. Woch.*, 1911, 2389; *Berlin. Klin. Woch.*, 1912, 4) that compounds of selenium and tellurium exert an electrical action on the cells of living organisms, and it is now found that the radium "adsorption" compounds of selenic, selenious, telluric, or tellurous acids, with salts of the alkalis, or alkaline earths, have an eminently specific action on tumour cells. *Radium barium selenate* is precipitated when radium barium chloride (0.4 mg.) in 0.16 c.c. of water is treated with 0.35 c.c. of *N*-barium chloride solution and 0.35 c.c. of *N*-sodium selenate; the filtrate is also radioactive. The preparation of *radium barium selenite*, *radium barium telluric acid*, *radium barium tellurite*, and of *radium sodium selenate* is also described.

F. M. G. M.

**The Radium Content of Pitchblendes.** BERTA HEIMANN and WILHELM MARCKWALD (*Physikal. Zeitsch.*, 1913, 14, 303—305).—In view of the results obtained by Gleditsch (A., 1911, ii, 845) according to which the ratio of radium to uranium varies quite appreciably in pitchblendes and related minerals, the authors have made a detailed examination of a number of pitchblendes from different sources. The method employed in the estimation of the radium content was similar to that described previously by Marckwald and Russell (A., 1911, ii, 360). The pitchblendes

examined were from East Africa, Norway (two samples), Joachimsthal, Marienberg, Freiberg, Příbram, Colorado, and Cornwall; and Bröggerite from Norway was also included in the series. The percentage of uranium in these minerals was found to vary from 9.01 in pitchblende from Cornwall to 71.2 in that from East Africa. The values obtained for the ratio of radium to uranium vary from  $3.320$  to  $3.341 \times 10^{-7}$ , the maximum deviation from the mean being less than 0.4%. The results are considered to prove conclusively that the ratio of the two elements in the primary minerals is quite constant, the mean value of the ratio being  $3.329 \times 10^{-7}$ .

In the case of six of the pitchblendes, the radium content was also estimated on the basis of their  $\gamma$ -ray activity, and in this way independent evidence was obtained in support of the constancy of the ratio.

On account of this relation, it is possible to make use of any pitchblende as a radium standard, and the employment of a mineral substance presents certain advantages over the use of an artificially prepared material. Apart from the question of impurities in the mineral standard, it is pointed out that the definition of the curie in terms of one gram of radium affords a unit which is much too large for convenient use in actual experimental work. As an alternative, the authors suggest that the curie should be defined as the quantity of radium emanation which is in equilibrium with one gram of uranium.

II. M. D.

**Chemical Properties of Thorium C and Thorium-D.** WALTHER LETZNER (*Ber.*, 1913, 46, 979—989).—Experimental investigations of the properties of thorium-C and -D have given results in complete agreement with the theoretical views of Fajans and others (*A.*, 1913, 276, 277). By the use of Strömhölm and Svedberg's method of crystallising fairly soluble salts out of a solution of the active deposit and by other methods, it has been shown that thorium-C cannot be separated from bismuth, or thorium-D from thallium. The quantitative separation of thorium-C by means of nickel foil in a boiling hydrochloric acid solution is hindered by the presence of bismuth, but the fraction of the radio-element precipitated on the foil is the same as the fraction of the bismuth also precipitated. Similarly, the volatilisation is stopped if bismuth oxide is present. Precipitation of thorium-C by silver chloride or bromide is prevented by addition of bismuth. The proportion of thorium-C in the precipitate and filtrate is shown to be the same as that of the bismuth when the latter, in presence of thorium-C, is fractionally precipitated (1) as oxychloride, (2) as bismuth magnesium nitrate, (3) as basic bismuth nitrate. Thorium-D, separated by recoil, was dissolved and crystallised with thallium salts. The proportion of the radio-element in the crystals and mother liquor was the same as the proportion of thallium, no separation or concentration being effected. Thallous nitrate, thallous carbonate in dilute ammonia solution, and thallic ammonium sulphate were the salts crystallised.

F. S.

**Chemical Action of Thorium-X on Organic Substances, Especially on Uric Acid.** WILHELM FALTA and L. ZEHNER (*Chem. Zentr.*, 1913, i, 639; from *Berlin. Klin. Woch.*, 1912, 44, 2444—2449).—Thorium-X solution glows in the dark, reacts acidic, and 1 c.c. has an activity of 1000 electrostatic units. Its action on organic substances is entirely due to radiation, and since the disintegration of thorium-X compared with that of radium emanation is almost explosive in character, the effect is very considerable.

Easily oxidisable aniline dyes and arrowroot-starch-iodine solutions are bleached; alcoholic guaiacol solution becomes blue; alcin solution, red; permanganate is decomposed. Solutions of morphine and pilocarpine hydrochlorides, strychnine nitrate, atropine sulphate, sodium salicylate, and antipyrine become very dark in colour, and quinine sulphate becomes green; the solutions suffer in pharmacological value. Tyrosine solutions deposit a black precipitate; catechol solution becomes dark; homogentisic acid solution gives a brown colour and a black precipitate; solutions of resorcinol become yellow, and of adrenaline, red. Starch and albumin are hydrolysed, and uric acid salts are rendered more soluble, and are even chemically changed. J. C. W.

**Apparatus for Study of the Activity of the Air of the Sub-soil.** JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1913, 11, 165—166).—Porous cylinders surrounded by earthenware vessels, to which iron tubes of 10—12 mm. are sealed, are sunk at 0.5, 1, and 2 metres below the surface. G. D. L.

**Activity of the Air of the Sub-soil in October, 1912.** JOSÉ MUÑOZ DEL CASTILLO and JOSÉ BARRIO Y FERNÁNDEZ (*Anal. Fis. Quim.*, 1913, 11, 225—234).—Numerical data over the period in question. At a depth of 0.5 metre the activity appears greater in a firm than in a loose soil, and up to 2 metres the activity increases with the depth. G. D. L.

**Analytical Observation on the Activity of Rain Water** JOSÉ MUÑOZ DEL CASTILLO and JOSÉ BARRIO Y FERNÁNDEZ (*Anal. Fis. Quim.*, 1913, 11, 167—168).—A certain sample of rain water contained a notable amount of emanation, which was extinguished according to Curie's law, and ions which disappeared after twelve days in a closed bottle. G. D. L.

**The Electromotive Series of the Radioactive Elements** I. GEORG VON HEVESY (*Zeitsch. Elektrochem.*, 1913, 19, 291—295; *J. Radium*, 1913, 10, 65—69. Compare A., 1912, ii, 414).—The various methods which can be used for the determination of the position of the radioactive elements in the electromotive force series are discussed, and it is shown that in the case of elements of short lives the only practicable method is the electrochemical one. This consists in the determination of the relation in which two radioactive elements (for example, Ra-A and Ra-B) are deposited from solution on to an electrode at a constant potential. The knowledge

of the chemical characteristics of the elements Ra-D and Th-B enables the elements of short and long lives to be brought into the electromotive series. The electromotive series of the radioactive elements contains both strongly electro-positive and strongly electro-negative members just in the same way as the series for the commoner elements. It is shown that every radioactive change, whether it consists in the emission of an  $\alpha$ - or a  $\beta$ -ray, leaves behind an atom the position of which in the electromotive series is far removed from that of the parent substance. From the last fact the author draws the conclusion that the chemical properties of the atoms depend to a large extent on the configuration of the electron rings in the atom, and he points out that in the radioactive elements we have "isomeric atoms," the different properties of which are due to the different special arrangement of the electron rings in the same way that the properties of isomeric molecules are conditioned by the different arrangements of the atoms in the molecules. J. F. S.

**Influence of Temperature and Pressure on the Electrical Resistance of Metals.** EDUARD GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1913, 15, 186—200).—By reference to the data for copper, silver, platinum, gold, and lead, it is shown that the specific electrical resistance of the pure metals at low temperatures is a universal function of  $T/\beta\nu_m$ , where  $T$  is the absolute temperature,  $\beta$  the radiation constant, and  $\nu_m$  the characteristic frequency of vibration of the atoms of the metal.

It has also been found empirically that the ratio of the resistivity to the absolute temperature is at low temperatures proportional to the atomic heat. This relationship may be expressed in a different way, namely, that the rise of temperature produced in a thermally isolated metallic conductor during the time interval  $dt$  is proportional to the square of the current and to the absolute temperature of the metal.

Although Wien's theory does not satisfactorily represent the influence of temperature on the electrical resistance, it is shown that the variation of the resistance with pressure is in harmony with the view that the mean free path of the electrons is inversely proportional to the square of the amplitude of the vibrating atoms. The observed diminution of the resistivity on increase of pressure is found to agree quite well with that calculated on the basis of this theory in the case of aluminium, copper, silver, cadmium, and gold. For nickel, platinum, and lead, the agreement is not so good. The effect of pressure on alloys, which consist of solid solutions, is also expressed by Wien's formula. H. M. D.

**The Selective Photo-electric Effect in Reference to Absorbed Light Energy.** ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1913, 15, 173—185. Compare A., 1910, ii, 922; 1911, ii, 787; 1912, ii, 317).—If the photo-electric current emitted by the alkali metals when acted on by ultra-violet radiation is represented as a function of the wave-length, and the effect referred to unit quantity of absorbed energy instead of to unit quantity of



incident energy, it is found that the resonance maximum becomes much more sharply developed. The quantity of electricity which is set free when a quantity of energy equal to one calorie is absorbed in the middle of the resonance region amounts to  $50 \times 10^{-4}$  coulombs in the case of potassium, and  $120 \times 10^{-4}$  coulombs for sodium. Higher values for the electric discharge per unit of absorbed energy are obtained if the data for the coloured colloidal modifications of the alkali metals are employed in the calculation; for both potassium and sodium the observations indicate that the photo-electric discharge is of the order of  $350 \times 10^{-4}$  coulombs per calorie when the incident rays correspond with the middle of the resonance region.

From a comparison of the numbers representing the photo-electric effect referred to unit quantity of incident and absorbed energy respectively, it is found that the region of the selective effect is characterised by the fact that the metal has a high reflexion capacity towards rays of this wave-length.

H. M. D.

**Electrical Conductivity of Bromine Solutions of Iodine.** VLADIMIR A. PLOTNIKOV and V. E. ROKOTJAN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 193—199. Compare A., 1904, ii, 156).—The authors have measured the conductivities of solutions of iodine in bromine with concentrations of 0—44.5% of iodine (or 72.28% of BrI) at 25°, and of 44.5—59.48% of iodine at 40.6°. The specific conductivity at 25° increases continuously from  $\chi_{25} \cdot 10^6 = 0.32$  for 12% of iodine to 126 for 44.5% of iodine. The molecular conductivity diminishes uninterruptedly with increase of dilution. With rise of temperature the conductivity increases, the extent of the change being greater for dilute than for concentrated solutions.

These results are explained by the formation of an iodine bromide (compare Bruner and Bekier, A., 1912, ii, 732) and its dissociation into bromine and iodine ions.

The marked electrical conductivity of bromine solutions of iodine does not agree with the view that conductivity is conditioned by appreciable increase in the dielectric constant of the solvent.

Comparison of conducting solutions of iodine in bromine with non-conducting solutions of potassium bromide in bromine indicates the invalidity of the hypothesis which regards electrolytes as divisible into "good" or "typical," such as potassium bromide, and "bad." Electrical conductivity must, indeed, be considered as a consequence of the electrochemical relations of the solute with the solvent.

T. H. P.

**Electrical Conductivity and Fluidity of Strong Solutions.** WILLIAM SANSONE TUCKER (*Proc. Physical Soc. London*, 1913, 25, 111—122).—Measurements have been made of the viscosity and electrical conductivity of concentrated solutions of calcium chloride at temperatures between  $-50^\circ$  and  $85^\circ$ .

At constant temperature ( $16.77^\circ$ ) the conductivity increases with the concentration, attains a maximum, and then diminishes. The maximum corresponds with a solution containing about 5 mols. of

calcium chloride per 100 mols. of water. If the ratio of the conductivity ( $C$ ) to the fluidity ( $F$ ) is plotted as a function of the concentration ( $n$ ), expressed in mols. salt per mols. of water, a straight line is obtained which passes through the origin. In other words, the value of  $C/n \cdot F$  remains practically constant for values of  $n$  between 1 and 16.6. The data obtained by Bousfield and Lowry for concentrated solutions of sodium hydroxide (A., 1905, ii, 135) are shown to exhibit the same relationship.

The curves obtained by plotting the conductivity and the fluidity as a function of the temperature are found to exhibit considerable differences. It is also found that the curves obtained by plotting  $C/n$  as a function of the temperature vary considerably according to the value of  $n$ . When  $n$  is small, the curves are very nearly straight lines, but increasing curvature is developed as  $n$  increases. There is no evidence of the existence of a temperature at which the conductivity would become equal to zero, as has been suggested by Lyle and Hosking for sodium chloride solutions (A., 1902, ii, 440).

H. M. D.

**The Dissociation Constants of Certain Very Weak Acids, Especially the Carbohydrates, Measured by Electrometric Methods.** LEONOR MICHAELIS and PETER ROSA (*Biochem. Zeitsch.*, 1913, 49, 232–248).—If an acid is added to a given solution of a base, the hydroxyl ion concentration is diminished, which diminution can be readily measured electrometrically. The acid dissociation constant  $K = [S'] \cdot [H]/[S - S']$  when  $[H]$  = hydrogen ion concentration of the mixture,  $S'$  the concentration of the acid ions,  $S$  = the total quantity of added acid. All these constants are readily measured, as  $S'$  is the difference of hydroxyl ion concentration of the alkali before and after the addition of acid. A correction, which is small in the case of weak acids, must be made for the dissociation of the sodium salts. If  $\gamma$  = the dissociation grade, then  $K = [S'] \cdot [H]/[S - \gamma[S']]$ . To carry out the measurements, the concentration of the alkali should not exceed 0.03N, and potassium chloride to the amount of 0.1N should be added, the interposed liquid between the electrodes being a saturated solution of this salt. The diffusion potential in this case is reduced to a minimum. The sodium hydroxide used must be quite free from carbonate, and the method is not available, owing to small changes produced on addition of the acid, when  $K < 10^{-15}$ . By this method, the following values for  $K$  were obtained: Phenol,  $5.8 \times 10^{-11}$ ; glycine  $k_a$ ,  $1.2 \times 10^{-10}$ , and  $k_b$ ,  $1.9 \times 10^{-12}$ ; glycerol,  $0.7 \times 10^{-14}$ ; sorbitol,  $2.5 \times 10^{-14}$ ; mannitol,  $3.4 \times 10^{-14}$ ; dulcitol,  $3.5 \times 10^{-14}$ ; arabinose,  $3.7 \times 10^{-13}$ ; dextrose,  $6.6 \times 10^{-13}$ ; galactose,  $5.3 \times 10^{-13}$ ; levulose,  $8.8 \times 10^{-13}$ ; mannose,  $10.9 \times 10^{-13}$ ; sucrose,  $2.40 \times 10^{-13}$ ; lactose,  $6.0 \times 10^{-13}$ ; maltose,  $18.0 \times 10^{-13}$ ; and raffinose,  $1.8 \times 10^{-13}$ .

S. B. S.

**An Improved Method for the Electrometrical Measurement of the Reaction of Biological Liquids.** KARL A. HASSELMANN (*Biochem. Zeitsch.*, 1913, 49, 451–457).—Liquids which contain dissociable oxygen compounds, or which are relatively poor in

"buffer" substances, cause certain difficulties when the reaction is electrometrically measured by the author's shaking method, as previously described (A., 1911, ii, 182). These can be overcome, however, by permanent shaking and constant washing of the electrodes by the liquid, by the use of a modified apparatus, which is described in detail and figured in the text. S. B. S.

**The Conditions which Determine the Cathodic Overvoltage.** JOHN N. PRING (*Zeitsch. Elektrochem.*, 1913, 19, 255-262. Compare Pring and Curzon, *Trans. Faraday Soc.*, 1912, 7, 237; Tafel, A., 1912, ii, 223).—The various theories concerning overvoltage on metallic surfaces are discussed, and a series of experiments is recorded showing the influence of various thicknesses of electrolytically deposited metals on various cathodes. The following cathodes and coatings were investigated: Copper coated with zinc; nickel coated with lead; nickel coated with zinc; nickel coated with tin; zinc coated with copper; platinum coated with copper; zinc coated with gold; copper coated with platinum. The potential measurements show that thin metallic layers on the cathode have a definite influence on the overvoltage, and that the influence depends on the thickness of the layer. For each metal there is a maximum thickness, above which an increase in thickness has no effect on the overvoltage. The maximum value is obtained whether the cathode itself has a higher or lower value than the surface layer. The thickness is the same as that to which the hydrogen penetrates the cathode at decomposition. The thickness for the various coatings are: platinum,  $4 \times 10^{-6}$  mm.; gold,  $1.6 \times 10^{-4}$  mm.; zinc,  $4.2 \times 10^{-4}$  mm.; copper,  $3.4 \times 10^{-3}$  mm.; tin,  $5.5 \times 10^{-3}$  mm.; nickel,  $1.6 \times 10^{-2}$  mm.; and lead,  $6.6 \times 10^{-2}$  mm. J. F. S.

**Phenomena at the Anode in Discharge Through Gases.** WALTER G. CADY (*Physikal. Zeitsch.*, 1913, 14, 296-302).—Certain changes are described which have been found to take place in the positive column on the passage of the discharge through nitrogen in tubes provided with anodes of copper, mercury, iron, or silver. The phenomenon consists in a contraction of the positive glow in such a way that the discharge at the anode surface appears to be focussed in a number of centres. The effect is supposed to be due to the formation of small patches of oxide as a consequence of the presence of traces of oxygen in the tubes, but it is probable that other foreign substances on the anode surface may give rise to the same phenomenon. In this connexion the author discusses changes in the character of the discharge which have been noted by previous observers, and an attempt is made to correlate the phenomena. H. M. D.

**Transport Numbers in Antimony Trichloride as Solvent.** KASIMIR FRYCZ and STANISLAS TOLLOCZKO (*Chem. Zentr.*, 1913, i, 91; from *Festschr. Univ. Lemberg*, 1912, 1, 1-16).—In continuation of the study of antimony trichloride as an ionising solvent (Tolloczko, A., 1909, ii, 190; 1901, ii, 437; Klemensiewicz, A., 1908, ii, 1013), the

transport numbers of solutions of ammonium and potassium chloride have been measured at 99°. The results show that, with increasing dilution, the transport numbers increase much more rapidly than is the case in aqueous solution, and the general rule is confirmed that the ions which have the higher transport numbers are those that are common to the electrolyte and the solvent, in this case the chlorine ions.

J. C. W.

**The Magnetic Properties of Some Solid Hydrates of Copper and Chromium.** (Mlle.) E. FEYTS (*Compt. rend.*, 1913, 156 886—889. Compare A., 1911. ii, 1058).—A study of the coefficient of magnetisation of the hydrates of cupric chloride and its double chlorides with sodium, potassium, and ammonium shows that the molecular coefficients for the hydrates cannot be obtained additively from that of water and the anhydrous salt. The molecular coefficients of magnetisation of the anhydrous salts, having a brown colour, group themselves round the value  $1230 \times 10^{-6}$ , and those of the hydrates, green or blue, round  $1400 \times 10^{-6}$ .

In the case of the hydrates of chromium chloride and sulphate and the double sulphates of chromium and potassium, no difference is found between the specific coefficients of magnetisation of isomeric violet and green hydrates. With the exception of anhydrous chromic chloride, all the chromic salts have practically the same molecular coefficients of magnetisation.

W. G.

**The Magnetism of Anhydrous and Hydrated Salts.** (GÉROISE WYROUBOFF (*Compt. rend.*, 1913, 156, 1072—1074. Compare A., 1902, 565, 609).—A claim for priority over Feyts (preceding abstract).

W. G.

**[Magnetic] Susceptibility of Iron, Steel, Nickel, and Cobalt at Higher Temperatures** KÔTARÔ HONDA and HIROMI TAKAGI *Sci. Reports Tôhoku Imp. Univ.*, 1913, 1, 229—242).—The magnetic susceptibility was examined at temperatures up to about 1300°. The results are exhibited in the form of curves in which the reciprocal of the susceptibility is plotted as a function of the temperature. The general conclusion drawn from the data is that Curie's law is only applicable to definite and limited intervals of temperature.

In the case of nickel, the agreement is good above 500°, but slight deviations are found at lower temperatures. For cobalt the deviations from Curie's law are more marked. The curve is convex towards the temperature axis below 1240°, but above this the points lie on a straight line. In the case of  $\beta$ -iron, the law is only approximately satisfied, and for  $\gamma$ -iron the data diverge very widely from the theoretical requirements.

From the data for a number of steels containing different amounts of carbon, it appears that in the  $\beta$  condition there is approximate agreement; the divergence from the law increases, however, with the carbon content, and the law is evidently not applicable to steels in the  $\gamma$  condition.

H. M. D.

**Saturation Curves and the Law of the Corresponding States.** EMILE H. AMAGAT (*Compt. rend.*, 1913, 156, 843—848).—An extension of the work already published (compare this vol. ii, 188), the curves being given for very low pressures and also for other substances. The results obtained bear out the previous work and conclusions. W. G.

**Adiabatic Expansion in Liquids.** L. GAY (*Compt. rend.*, 1913, 156, 1070—1072).—The author has determined the dilatation produced in liquids by adiabatic expansion from a pressure of two atmospheres to one in the case of mercury, water, and benzene, in an apparatus described in detail in the paper. From his results he has calculated the value of  $\beta$ , the isothermal coefficient of compressibility, by means of the formula  $\beta = \gamma + T\alpha^2/41.3cD$ , where  $\gamma$  is the adiabatic coefficient of compressibility, obtained experimentally,  $\alpha$  the thermal coefficient of dilatation,  $c$  the specific heat at constant pressure, and  $D$  the density. The results obtained are in fairly close agreement with those already given by Amagat (compare A., 1909, ii, 549). W. G.

**Method for Determining the Latent Heat of Evaporation of Metals.** CR. MUSCÉFANU (*Bull. Acad. Sci. Roumaine*, 1912 13, 1, 145—151).—The principle of the method adopted consists in electrically heating the metal to its temperature of evaporation, and measurement of the heat employed and weight of metal volatilised. The following results were obtained: mercury, 63.66 cal.; cadmium, 181.0 cal.; zinc, 365.8 cal.; magnesium, 1700.0 cal.; bismuth, 161.5 cal., the pressure in each case being  $2 \cdot 10^{-3}$  mm. of mercury. H. W.

**A Relation between the Boiling Points and Molecular Weights of the Members of Homologous Series.** SAMUEL SUGGS (*Chem. News*, 1913, 107, 135—136. Compare J. C. T., A., 1912, ii, 1136).—Starting with van der Waals' equation, and assuming that liquefaction will take place when the internal attraction of the particles for each other surpasses a critical value, that is, when  $a/V^2 = K$ , the author deduces that  $\alpha\sqrt{a} - \beta h = T$ , where  $a$  and  $b$  are the constants in van der Waals' equation,  $T$  is the boiling point at constant pressure, and  $\alpha$  and  $\beta$  are constants. Now  $\alpha$ , the coefficient of attraction between the molecules, is proportional to their mass  $M$ , and  $b$  is probably also a function of  $M$ , and, for members of a homologous series, may be considered to vary as  $M$ . It follows therefore that the boiling points of the members of a homologous series should be connected by the relation:  $T = A\sqrt{M} - BM$ , where  $A$  and  $B$  are constants. If  $B$  is small compared with  $A$ , the relation reduces to the form  $T/\sqrt{M} = \text{constant}$ , which is that found by J. C. T. (*loc. cit.*), and this is found to hold in the case of the normal paraffins, the value of the constant being  $37.2 \pm 0.01$ . In the following series the value of  $A$  (given in brackets) is deduced from the relation  $T = A\sqrt{M} - BM$ , and found

to be constant: normal fatty acids ( $66.5 \pm 0.2$ ); methyl esters of the fatty acids ( $42.8 \pm 0.1$ ); alcohols,  $C_nH_{2n+1}OH$  ( $83.3 \pm 0.5$ ); ethers,  $C_nH_{2n+2}O$  ( $35.9 \pm 0.15$ ); aldehydes,  $C_nH_{2n+1}CHO$  ( $50.3 \pm 0.2$ ); ketones,  $(C_nH_{2n+1})_2CO$  ( $50.4 \pm 0.3$ ). T. S. P.

**Vapour Pressures of the Alkali Metals.** A. KRÖNER (*Ann. Physik*, 1913, [iv], 40, 438—452).—The vapour pressures of potassium and caesium have been determined at temperatures between  $250^\circ$  and  $400^\circ$  by a method involving the measurement of the change in volume which occurs when the heated metal is brought into communication with an indifferent gas and the total pressure is kept constant. When the data are combined with the vapour pressure values for sodium, which Gebhardt (A., 1906, ii, 9) obtained by measuring the boiling point at different pressures, it is found that the vapour pressure-temperature relationships are in agreement with the Ramsay-Young rule for closely related substances.

The method of vapour pressure measurement employed by the author can only be applied when the pressure is small, but by making use of the data for sodium, which extend over a much larger range of pressures, it is possible to calculate the vapour pressures of the other alkali metals over the corresponding range by making use of the boiling-point data for atmospheric pressure and the validity of the Ramsay-Young rule. H. M. D.

**Ionic Size in Relation to Molecular Physics. Together with a New Law Relating to the Heats of Formation of Solid, Liquid, and Ionic Molecules.** WILLIAM R. BOESFIELD (*Proc. Roy. Soc.*, 1913, A, 88, 147—169. Compare A., 1905, ii, 369; 1906, ii, 428).—By reference to the data for compounds containing hydrogen, potassium, sodium, or lithium in combination with chlorine, bromine, iodine, or the groups  $NO_3$  or  $IO_3$ , it is shown that the heat of combination, in the liquid or solid state, of any of the electro-positive elements with any of the electro-negative elements or radicles is approximately equal to the sum of certain constants peculiar to the two elements or radicles, together with  $0.875\delta I$ , where  $\delta I$  is the change of atomic volume produced by the combination. This result may be expressed in the form  $\Sigma = H_1 + H_2 + 0.875\delta I$ . In order to be able to assign definite values to  $H_1$  and  $H_2$ , it is necessary to give an arbitrary value to some one element, but this makes no real difference to the additive nature of the relationships which are involved. The heats of formation of the halogen compounds of calcium, strontium, barium, zinc, and cadmium can be represented in a similar manner.

According to the data for the chlorides of lithium, sodium, and potassium, it appears that the heat of ionisation is similarly connected with the change in volume which occurs when the elements pass into the ionic condition. If  $n$  is the number of water molecules which are chemically combined with the dissolved salt, and if a calorific constant 1.85 is assigned to each molecule of combined water; then the heat of ionisation of the three salts can be represented by:  $\Sigma = 0.875\delta I + 1.85n + 46.6$ . This expression may be

modified and combined with the previous one, so as to obtain a formula which is applicable to the heats of formation of both solid salts and ionised salts.

In regard to the significance of the term  $0.87581V$ , it is supposed that this affords a measure of the diminution in the internal energy which results from the contraction occurring on combination.

An empirical relation between ionic volume and freezing point depression has been found, which may be written in the form  $1/D = p - qN(I_v - K)$ , where  $D$  is the effective molecular freezing-point depression,  $N$  the number of mols. of solute per 1000 grams of water,  $I_v$  the ionic volume, and  $K$  the volume of the ionic nuclei, and  $p$  and  $q$  are constants. By combining this with the empirical relation  $EV_v = a - bI_v$  ( $a$  and  $b$  being constants and  $EV_v$  the molecular solution volume of the electrolyte; see previous papers, *loc. cit.*), it is shown that numbers may be obtained which represent the molecular hydration of the dissolved salt. The values for lithium, sodium, and potassium chlorides, obtained in this way, are 21, 13, and 9 respectively. In combination with Washburn's data, obtained from transport measurements (A., 1908, ii, 1009), this leads to the following hydration values for the various ions: Cl, 4; K, 5 Na, 9; and Jd, 17.  
H. M. D.

#### Heats of Combustion and Transformation of Some Elements.

**I. Diamond and Graphite.** WALTER A. ROTH and H. WALLASCH (Ber., 1913, 46, 896—911).—The determinations were carried out in a bomb calorimeter, using liquid paraffin as the addition agent to bring about complete combustion. The graphite used was both natural and artificial (Acheson), and before use it was purified by treatment with two or more of the reagents: hydrochloric acid, nitric acid, hydrofluoric acid, chlorine. The purer it was, the greater was the heat of combustion.

The heat of combustion of one gram of diamond ( $D^{18}=3.50$ ) was found to be  $7869 \pm 3$  gram-cal., in very good agreement with the corrected value ( $7869 \pm 2$ ) of Berthelot and Petit. For graphite, the value found was  $7851 \pm 1$  gram-cal.; in most cases this value was independent of the source of the graphite, but with certain natural graphites a value 0.3% lower was obtained. The results for graphite are thus lower than for the diamond, in contradistinction to the results obtained by Berthelot and Petit with graphite obtained from a blast furnace.

The thermochemical measurements show that the distinction which has been made between graphite and graphitite cannot be maintained.

When finely divided graphite or lamp-black is mixed with liquid paraffin, there is a slight development of heat, which, however, is not sufficient to make any difference in the heats of combustion.

Purified graphite obtained from cast iron or from the blast-furnace gave the values 7855–7865 gram-cal. per gram, in agreement with the numbers given above, and in disagreement with the value of Berthelot and Petit.  
T. S. P.

**Calorimetric Study of the Iron-Carbon System.** A. MEUTHEN (*Ferrum*, 1912, 10, 1—21).—The total heat-content of a series of iron-carbon alloys between the limits 0.06 and 4.03% of carbon and 650° and 920° has been determined by means of the vacuum calorimeter. The heat of transformation of pearlite, containing 0.9% C, is 15.9 Cal. per gram, and that of  $\beta$  into  $\alpha$ -iron 5.6 Cal. per gram. One gram of  $\alpha$ -iron separating from solid solution develops 14.1 Cal. per gram. The horizontal line in the equilibrium diagram, which represents the transformation of  $\beta$  into  $\alpha$ -iron, does not extend beyond 0.32% C. Within the limits 650–700°, the heat-content of the alloys is not directly proportional to the carbon concentration, but the curve consists of two straight lines, intersecting at a considerable angle at a concentration just above that of pearlite.

C. H. D.

**Heats of Combustion of Cyclic Compounds.** II. PAVEL V. ZENOV (*J. Russ. Phys. Chem., Soc.*, 1913, 45, 240—251).—With reference to the data published in the author's first paper (A., 1902, i, 144), the following remarks are made: Methylcyclohexene ( $\beta$ ) has been shown by Zelinski to be a mixture of isomeric hydrocarbons; methylcyclohexene ( $\alpha$ ) is 1-methyl- $\Delta^3$ -cyclohexene;  $C_7H_{12}$ .CHMe.OH is probably methylcyclohexylmethylcarbinol;  $C_7H_{12}$ .COMe is probably methyl methylcyclohexyl ketone; 1:1:5-trimethylcyclo-5-hexene-3-one is more correctly termed 1:1:3-trimethyl- $\Delta^3$ -cyclohexene-5-one (*isophorone*).

The following new results have been obtained, the numbers referring to Cals. per gram-molecule:

#### Hydrocarbons.

		Constant volume.	Constant pressure.
$C_4H_{10}$	Methylcyclobutane .....	756.5	782.0
	cyclopentane .....	759.9	781.4
$C_5H_{12}$	Methylcyclopentane .....	945.7	917.4
	cyclohexane .....	943.4	915.1
$C_6H_{14}$	1:3-Dimethylcyclopentane .....	1029.5	1101.5
	Methylcyclohexane .....	110.08	1102.8
	cycloheptane .....	1090.3	1098.3
$C_7H_{16}$	1:2:4-Trimethylcyclopentane .....	1255.7	1258.0
	1:1-Dimethylcyclohexane .....	1252.8	1255.1
	1:3-Dimethylcyclohexane .....	1248.1	1250.4
	1:4-Dimethylcyclohexane .....	1238.9	1241.2
	Methylcycloheptane .....	1251.8	1257.1
$C_8H_{18}$	1-Methyl-3-propylcyclopentane .....	1412.9	1415.5
	1:2:3-Trimethylcyclohexane .....	1407.3	1409.9
	1:3:3-Trimethylcyclohexane .....	1406.0	1408.6
	Ethylcycloheptane .....	1418.3	1420.9
$C_9H_{20}$	1-Methyl-3-propylcyclohexane .....	1563.6	1566.5
	Carvomenthane .....	1527.0	1529.9
$C_9H_{18}$	Dimethylmethylcyclopentane .....	905.6	907.1
	cyclohexene .....	808.9	800.1
$C_9H_{12}$	1-Methyl- $\Delta^3$ -cyclohexene .....	1049.8	1051.5
	1-Methyl- $\Delta^4$ -cyclohexene .....	1052.4	1054.1
	Methyl-6-methylcyclohexane .....	1052.9	1054.6
	Dicycloheptane .....	1049.1	1050.8
	1-Heptene .....	1058.7	1060.1



*Hydrocarbons (continued).*

		Constant volume.	Constant pressure.
$C_5H_{14}$	1:1:2 Trimethyl- $\Delta^2$ -cyclopentene ( <i>isolaurelene</i> )	1203.4	1205.1
	Laurelene .....	1202.8	1204.8
	1:3-Dimethyl- $\Delta^2$ -cyclohexene .....	1204.6	1206.6
$C_{10}H_{18}$	Fenchene .....	1515.3	1517.9
$C_{12}H_{20}$	Hexahydro- <i>m</i> -ditolyl .....	2123.5	2127.3
$C_{12}H_{18}$	$\Delta^{1:3}$ -Dihydrobenzene .....	840.6	841.7
$C_{12}H_{18}$	1:3-Dimethyldihydrobenzene ..	1158.2	1159.9
$C_{10}H_{16}$	<i>l</i> -Limonene .....	1469.7	1472.0
$C_{10}H_{16}$	<i>l</i> -Pinene .....	1485.7	1488.0
	<i>d</i> -Pinene .....	1484.4	1486.7

*Alcohols.*

$C_4H_{10}O$	<i>cyclo</i> Butylcarbinol .....	754.2	755.4
$C_5H_{12}O$	1-Methyl-2- <i>cyclopentanol</i> .....	895.1	896.6
	<i>cyclo</i> Hexanol .....	897.3	898.8
$C_5H_{12}O$	1-Ethyl-2- <i>cyclopentanol</i> .....	1047.7	1049.1
	1:3-Dimethyl-2- <i>cyclopentanol</i> .....	1039.2	1040.9
	1:3-Dimethyl-3- <i>cyclopentanol</i> .....	1042.7	1044.4
	<i>cyclo</i> Hexylcarbinol .....	1056.0	1057.7
	1-Methyl-3- <i>cyclohexanol</i> .....	1047.2	1048.9
	<i>cyclo</i> Heptanol .....	1059.0	1060.7
$C_6H_{14}O$	1:3-Dimethyl-2- <i>cyclohexanol</i> .....	1206.0	1208.0
	1:3-Dimethyl-3- <i>cyclohexanol</i> .....	1202.5	1204.5
	1:3-Dimethyl-5- <i>cyclohexanol</i> .....	1193.1	1195.1
	1-Methyl-1- <i>cycloheptanol</i> .....	1199.4	1201.4
$C_6H_{14}O$	Methyl- <i>cyclohexylmethyl</i> carbinol .....	1353.4	1355.7
	1-Methyl-3-ethyl-3- <i>cyclohexanol</i> .....	1333.5	1335.8
$C_8H_{18}O$	1:3:5-Trimethyl- $\Delta^{4:5}$ - <i>cyclohexanol</i> .....	1305.9	1307.9
$C_7H_{16}O_2$	1:1-Dimethyl- <i>cyclopropane</i> .....	714.2	715.1

*Ketones.*

$C_5H_8O$	Acetyl- <i>cyclopropane</i> .....	697.5	698.3
$C_6H_{10}O$	Acetyl- <i>cyclobutane</i> .....	864.2	865.4
	1-Methyl-2- <i>cyclopentanone</i> .....	840.7	841.9
$C_7H_{12}O$	1-Ethyl-2- <i>cyclopentanone</i> .....	998.9	1000.4
	1:3-Dimethyl-2- <i>cyclopentanone</i> .....	998.3	999.3
	1-Methyl-3- <i>cyclohexanone</i> .....	1065.4	1064.9
	<i>cyclo</i> Heptanone .....	1005.1	1009.6
$C_8H_{14}O$	1:3-Dimethyl-2- <i>cyclohexanone</i> .....	1139.5	1141.2
$C_8H_{16}O$	Ethyl- <i>cyclohexyl</i> ketone .....	1360.7	1362.7
	1-Methyl-1-acetyl- <i>cyclohexane</i> .....	1278.8	1280.8
	Methyl-methyl- <i>cyclohexyl</i> ketone .....	1289.4	1291.4
$C_9H_{16}O$	1:3-Dimethyl- $\Delta^{4:5}$ - <i>cyclohexenone</i> .....	1111.8	1113.3
$C_9H_{16}O$	1:1:3-Trimethyl- $\Delta^{4:5}$ - <i>cyclohexenone</i> .....	1259.2	1260.9
$C_{11}H_{18}O$	Dihydrocarvone .....	1424.7	1426.7
	Carone .....	1409.2	1411.2

*Acids.*

$C_3H_6O_2$	<i>cyclo</i> Propanecarboxylic acid .....	488.3	488.6
$C_4H_8O_2$	<i>cyclo</i> Butanecarboxylic " .....	615.1	615.7
$C_6H_{10}O_2$	<i>cyclo</i> Hexanecarboxylic " .....	942.3	945.5
$C_7H_{14}O_2$	Hexahydro- <i>m</i> -toluic " .....	1095.6	1097.1
	A cyclic octoic acid from light petroleum (100-105°) .....	1095.6	1100.1
	Octoic acid from light petroleum (100-102°) ..	1091.1	1092.6
	<i>cyclo</i> Heptanecarboxylic acid .....	1096.3	1097.5

*Esters.*

		Constant volume.	Constant pressure.
$C_4H_9O_2$	Methyl cyclobutanecarboxylate .....	816.4	817.3
$C_7H_{15}O_2$	Ethyl 1-methyl-4-ethyl-3-cyclobutanone-4-carboxylate .....	1478.8	1480.5
$C_6H_{11}O_2$	Tricyclobutyrin .....	1862.1	1863.3
$C_8H_{15}O_2$	Tricyclovalerin .....	2329.8	2331.8

*Furan Derivative.*

$C_8H_{10}O$	4:4-Dimethyltetrahydrofuran .....	965.9	967.4
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*Nitrogen Compounds.*

$C_6H_6N$	...	...	...	...	...	...	830.2	831.5
$C_6H_6N$	...	...	...	...	...	...	1128.9	1129.9
$C_6H_6N$	...	...	...	...	...	...	1446.1	1446.6
$C_6H_6ON$	...	...	...	...	...	...	1375.3	1377.2

The above numbers are based on Regnault's value of the specific heat of water at 20°.

T. H. P.

**The Chemical Interpretation of Special Points on Curves.**

L. GAY and P. DUCELLIEZ (*Bull. Soc. chim.*, 1913, [iv], 13, 320—324).

—It is pointed out that the commonly accepted idea that a maximum or minimum point in a curve representing the relationship between a physical property and the composition of a mixture represents a definite compound of the components of the mixture is often erroneous, and in illustration it is shown that a number of curves with different maxima may be drawn, representing the relationship between density and composition of mixtures of acetic acid and water. Maximal points in melting-point curves of mixtures generally represent definite compounds, but in other cases a number of other factors must be considered before it can be assumed that a special point in the curve implies chemical combination (compare Band and Gay, A., 1909, ii, 558).

T. A. H.

**A Simple Method for Determining the Density of Mineral Powders.** MAURICE BILLY (*Compt. rend.*, 1913, 156, 1065—1067).

—The density of the powder is determined by weighing it in an aqueous solution of potassium hydroxide, the pycnometer used being previously exhausted and then filled with carbon dioxide prior to the introduction of the powder. A slightly modified form of stopper is shown and described, by means of which the flask is evacuated, filled with carbon dioxide, and finally gradually filled with the alkali. It is claimed that this method is quicker, and gives a far higher order of accuracy than the methods usually employed.

W. G.

**A Modified Victor Meyer Apparatus.** HAROLD CANNING

CHARN (*J. Ind. Eng. Chem.*, 1912, 4, 684).—A sketch with description of a modified Victor Meyer apparatus, in which the capsule containing the liquid (for the experiment) is made from a piece of 5 mm. glass tubing, sealed off at one end, and, after the liquid is

introduced, drawn into a capillary at the other, closed, and bent round twice at right angles; it is hung from the rod in the vapouring tube, a twist of which breaks the capillary and drops the capsule.

F. M. G. M.

**The Expansion Pressure of Normal Fluids.** L. GAY (*Compt. rend.*, 1913, 156, 1015—1017).—A mathematical paper in which the author, using Young's values for the physical constants of chloro-benzene, isopentane, diisopropyl, and cyclohexane (compare T., 1889, 55, 486), has verified his formula (compare A., 1911, ii, 1058) for the expansion pressure of liquids. For all the substances studied, the coefficient of compressibility is always less than  $(V-b)/V(P+K)$ , whence it follows that the internal pressure diminishes with the volume, the temperature remaining constant.

W. G.

**A New Physico-chemical Volumetric Method.** RÉSÉ DUBRISAY (*Compt. rend.*, 1913, 156, 891—898).—An application of Donnan's work (compare A., 1900, ii, 201) and its extension by Lewis (A., 1908, ii, 357) on the emulsion of oils, to determining the acidity of solutions. The method consists in determining the number of drops formed by the flow of a given volume of standard alkali from a pipette immersed in a given volume of the solution, the acidity of which it is required to determine. By varying the total volume of alkali run in, the number of drops shows a very marked and sudden increase when the alkali added is just sufficient to neutralise the acid. Figures and curves are given in illustration of the method.

W. C.

**A Simple Apparatus for the Absolute Measurement of the Coefficient of Viscosity of Gases and for the Demonstration of Maxwell's Law.** H. PIWNIKIEWICZ (*Physikal. Zeitsch.*, 1913, 14, 305—308). Compare Roberts, A., 1912, ii, 237).—A simple form of apparatus is described for the measurement of the viscosity of gases. It consists essentially of two small cylindrical gas reservoirs, connected by a capillary glass tube about 35 cm. long, the time required for the passage of a definite volume of gas through the tube being measured as well as the difference of pressure in the two reservoirs. The quantity of gas required is only a few c.c., and the measurement of the viscosity can be repeated as often as desired with the same material. The data obtained with air, carbon dioxide, and hydrogen show that the apparatus is capable of yielding accurate viscosity values.

It is also shown that the apparatus may be conveniently employed to demonstrate that the viscosity of a gas is independent of the pressure to which it is subjected.

H. M. D.

**Viscosities of the Systems: Chloral-Water and Chloral-Ethyl Alcohol.** NICOLAI S. KURNAKOV and N. N. FEREMOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 329—348).—For chloral the authors find  $D_{20}^{20}$  1.5049 (Perkin, T., 1887, 51, 809, gave 1.5060, and van Rossum, A., 1908, i, 501, 1.5030) and  $\eta_{20}$  0.01263. Two preparations of chloral hydrate gave  $D_{20}^{20}$  1.6193 and 1.6187 (Perkin, *loc. cit.*, found

1.6415 for the solid hydrate at  $50^{\circ}$ ,  $d_4^{20}$  1.5966 and 1.5946,  $D_4^{20}$  1.5148 and 1.5148, m. p. (slow heating)  $48.1^{\circ}$  (Perkin, *loc. cit.*, gave  $57.7^{\circ}$ , and van Rossem, *loc. cit.*,  $47.4^{\circ}$ ).

The viscosity isotherms of liquid mixtures of chloral and water at  $50^{\circ}$ ,  $60^{\circ}$ ,  $70^{\circ}$ ,  $85^{\circ}$ , and  $90^{\circ}$  are continuous curves exhibiting maxima, that of the  $50^{\circ}$  curve representing a viscosity nearly twenty times as great as that of the chloral, which is the more viscous constituent of the mixtures. The compositions at the maximal points are not constant for different temperatures, and do not correspond with rational proportions of the components; as the temperature is lowered, the molecular ratio 1:1 is indeed approached, but is not reached within the temperature limits of stable existence of the binary liquid phases. It is evident that the dynamic equilibrium of the system tends towards a limit depending on the formation of chloral monohydrate, which is accompanied by considerable development of heat.

These results are confirmed by the cryoscopic measurements of Beckmann (A., 1889, 11) and of Bruner (A., 1902, ii, 305), who found normal molecular weights for chloral hydrate in water, benzene, nitrobenzene, and *o*-toluidine, the values in acetic acid being less than the normal. At the solidifying temperatures of these solutions, below  $0^{\circ}$  to  $5.7^{\circ}$ , the dissociation of chloral hydrate is evidently so slight as to exert no appreciable influence on the magnitude of the molecular weight. Rise of temperature, however, increases the dissociation of the hydrate, and this is in agreement with the marked displacement of the viscosity maximum from the 50 mol. % point towards the water axis. The system chloral-water thus represents a typical example of the influence of hydration processes on the form of the viscosity diagram.

Similar relations hold for the temperature-coefficient of the viscosity. The curves showing the variation of this coefficient with composition for different ranges of temperature are of the same form as the viscosity isotherms, but the maxima are still more pronounced. The maxima correspond with 47.5 mol. % of chloral at  $50$ – $60^{\circ}$  and with 45 mol. % for  $60$ – $70^{\circ}$  and  $70$ – $85^{\circ}$ ; in the first case the coefficient is eighty-seven times as great as that for chloral. Here, too, the maximum never coincides with the molecular ratio 1:1, although this is approached as the temperature is lowered.

Chloral alcoholate,  $\text{CCl}_3\text{CHO}\cdot\text{Et}\cdot\text{OH}$ , m. p.  $45.2^{\circ}$  (Leopold, A., 1909, ii, 472, found  $46.6^{\circ}$ ), is highly hygroscopic, its specific gravity and viscosity being increased considerably by traces of water. For ethyl alcohol, the authors find  $D_4^{20}$  0.7900,  $D_4^{20}$  0.7818 (Doroshlevski gave  $D_4^{20}$  0.7893,  $D_4^{20}$  0.7809), and  $\eta_{20}$  0.01156 (Thorpe and Rodger, *Phil. Trans.*, 1894, 185, A, 379, gave  $\eta_{20}$  0.01192). Consequent on the smaller heat effect of the reaction between the components, the viscosity maxima for chloral-alcohol mixtures are considerably flatter than with chloral-water, but here, too, the position of the maximum approaches the 50 mol. % point as the temperature falls. When small proportions of water are present, the maxima approach very closely the above point, and are then but slightly displaced by change of temperature. The temperature-coefficient curves for

different ranges of temperature are similar to those obtained for water-chloral. T. H. P.

**Viscosity and Conductivity of Concentrated Solutions of Ferric Chloride.** ENRIQUE MOLES, M. MARQUINA, and G. SANTOS (*Anal. Fis. Quim.*, 1913, 11, 192—211).—Determinations of viscosity and conductivity of solutions of ferric chloride of from 0.025 to 8 molar strength at temperatures of 0°, 18°, 25°, and 35°.

G. D. I.

**Method for Determining the Surface Tension of Liquids for Biological Purposes.** C. C. ERDMANN (*J. Biol. Chem.*, 1913, 14, 141—147).—The apparatus described is based on that of Traube (*A.*, 1911, ii, 328). A drop pipette of a few c.c. capacity is provided with a highly polished drop surface, ground so as to form the base of a cone. Ten, 20, or more drops are collected and weighed. The results are expressed as drop numbers corresponding with 5, 10, or 50 grams of substance. Small amounts of acid cause a pronounced change in the surface tension of serum; similar amounts of alkali have very much less effect. A modified form of the apparatus is described for surface tension determinations of less dilute solutions.

On heating serum the surface tension changes very slowly at low temperatures, but rapidly at the beginning of coagulation, from 65—70°. There is, however, a break in the curve at 38°. E. F. A.

**Influence of Light on the Surface Tension of Various Solutions.** N. A. MARENINE (*J. Russ. Phys. Chem. Soc.*, 1913, 45, *Phys. Part*, 28—30).—A number of aqueous solutions of measured surface tension were subjected for either two or three minutes to the action of the light from a high-tension arc between aluminium electrodes, their surface tensions being then re-measured. Water and 3% magenta solution showed no change; 30% resorcinol solution showed a decrease of 9.6%, this being probably due to chemical changes; whilst 10% solutions of eosin, sodium sulphite, and potassium permanganate, and also 1% methyl-violet and 20% potassium nitrate solution, showed increases in surface tension varying from 3.2 to 5.1%.

Further measurements demonstrate that the increase in surface tension reaches a maximum approximately 1.5 minutes after the action of the light ceases. The surface tension subsequently falls continuously to the original value, which is sometimes attained only after thirty minutes.

A quartz mercury lamp of great actinic power does not cause any such increase in the surface tension, and it seems likely that the phenomenon is due to an action of electrical character. T. H. P.

**Independence of the Surface Tension of Light-sensitive Solutions on the Illumination.** NIKOLAI A. BISENIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, *Phys. Part*, 31—35).—The results of Marenine's experiments (compare preceding abstract) indicate that

the surface tension is not affected by the action of actinic rays. This conclusion is explained by assuming that these rays act solely on the stable nuclei of the electrons, and not on the external electrons of the atoms (compare Langevin, *J. Physique*, 1905). One of the consequences of Marenne's results is that actino-electric actions should be proportional to the concentrations of the solutions, and not, as G. C. Schmidt supposed from the results of his experiments with magenta solutions (*Ann. Physik*, 1898, **64**, 708), to the square-roots of the concentrations. Schmidt's experimental data are, however, in good agreement with the hypothesis that the ionic dissociation increases in inverse proportion to the square root of the concentration.

T. II. P.

Processes Operative in Solutions. XXV. Influence of Non-Electrolytes on Solubility. Nature of the Processes of Dissolution and Precipitation. HENRY E. ARMSTRONG and J. VARGAS EYRE (*Proc. Roy. Soc.*, 1913, **A**, 88, 234—245).—Measurements have been made of the solubility of lead chloride, silver acetate, and potassium chloride in water at 25° in presence of various non-electrolytes. The results indicate that no distinction can be drawn between the influence of non-electrolytes on the solubility of slightly soluble salts and that exerted on the solubility of readily soluble salts. The action of non-electrolytes and electrolytes on solubility appears to be of the same kind; in both cases the solubility may be diminished or increased. The experimental data are discussed from the point of view of Armstrong's theory relating to the constitution of water and aqueous solutions.

H. M. D.

Estimation of the Solubility of Solids in Liquids. PETR KUSNETZOV (*Chem. Zentr.*, 1913, **i**, 765; from *Izvesta Don. Polytech. Inst. Novotcherkusk*, 1912, **1**, ii, 399—410).—An improved form of Weimann's apparatus (*A.*, 1906, **ii**, 838) is described. By its means the solubility of manganese chloride,  $MnCl_2 \cdot 4H_2O$ , was found to agree with the values of Dawson and William (*A.*, 1900, **ii**, 210).

J. C. W.

The Formulation and Genetics of the Formation of Solid Solutions in the Dissociation of Oxides. SIEGFRIED BERGSTÄLLER (*Chem. Zentr.*, 1912, **ii**, 2005—2006; from *Abhandl. deut. naturwiss. med. Ver. Böhmen*, 1913, **3**, 147, 241).—The experiments of Wöhler (*A.*, 1911, **ii**, 259), Milbauer (*A.*, 1909, **ii**, 574, 589; 1910, **ii**, 291; 1911, **ii**, 113), and the author (this vol., **ii**, 57) lead to the assumption of solid solutions in the dissociation of oxides. According to the present views, a dissociating system, on the way towards equilibrium, passes from a system of three phases, gas, higher and lower oxide, by diffusion, into a system of gas and a solid phase composed of either a solution of the lower oxide or metal in the higher oxide or vice versa, or of two saturated solid solutions, according to whether the solids have the power of complete miscibility or form two series of mixed crystals.

J. C. W.

**Experimental Investigation into the Physical Conditions for the Crystallisation of Metals.** EMIL GURGEA (*Chem. Zentr.*, 1913, i, 677—678; from *Bul. Soc., Stiinta Bucuresti*, 1912, 21, 192—207).—When a porous pot containing a zinc rod is placed in a solution of copper sulphate, copper is deposited in the crystalline form on the outside of the cell. In the same way, lead may be deposited by zinc from lead acetate, and silver by copper from silver nitrate, in the form of crystals. The process has an application in the separation of one metal or another, as desired, from a mixture of different salts.

If a quantity of sand containing some metal powder or grains be moistened from below with copper sulphate solution, crystalline copper appears in the course of a few days, often with the accompaniment of copious gas evolution. This throws some light on the occurrence of metals with crystalline structure in the earth.

J. C. W.

**Phenomena of Crystallisation in Ternary Systems. VI. Cases with a Gap of Miscibility in the Liquid and also in the Solid State.** NICOLA PARRAVANO (*Gazzetta*, 1913, 43, ii, 220—237. Compare Parravano and Sirovich, A., 1912, ii, 836).—A continuation of this theoretical discussion.

R. V. S.

**Spontaneous Crystallisation and the Melting and Freezing point Curves of Two Substances which Form Mixed Crystals and the Freezing point Curve of which Exhibits a Transition Point.** Mixtures of *p*-Bromonitrobenzene and *p*-Chloronitrobenzene. (Miss) FLORENCE ISAAC (*Proc. Roy. Soc.*, 1913, A, 88, 205—216).—The freezing points of mixtures of these substances are all situated between the freezing points of the pure components, but the freezing-point curve consists of two branches corresponding with the formation of two different kinds of mixed crystals. The transition temperature corresponding with the intersection of the two curves is 84.5°, the mixture at this point containing 27.5% by weight of *p*-bromonitrobenzene.

The melting-point curve also consists of two branches, which correspond with the two types of mixed crystals. At the transition temperature, two solid phases may exist in equilibrium with the liquid mixture containing 27.5% of *p*-bromonitrobenzene, the solid phases containing 30 and 60% of the bromo-compound respectively. The two branches of the melting-point curve are consequently intercepted by a horizontal line which extends from 30 to 60 on its composition axis. Variation of the composition of the liquid between these limits changes the relative proportion of the two solid phases without altering the composition of either.

The supersolubility or spontaneous crystallisation curve has also been determined, and it is found that for each mixture there is a definite temperature at which spontaneous crystallisation occurs. This curve lies almost completely between the freezing- and melting point curves, and, like these, it shows a break in the neighbourhood of the transition point.

Microscopic observations relating to the pure substances and their mixtures are described. H. M. D.

The First Results of the Study of the Tables for Crystallo-chemical Analysis. EVGRAF S. FEDOROV (*Zeitsch. Kryst. Min.*, 1913, 52, 97—136. Compare A., 1912, ii, 772; this vol. ii, 305—306).—Further examples are quoted from the author's tables. Not suitable for abstraction. L. J. S.

A New Theory of the Phenomenon of Allotropy. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1913, 82, 657—664).—Polemical against Tammann's "Theory of Polymorphism" (this vol., ii, 193) (compare also A., 1910, ii, 195, 400). It is shown that the phenomena of enantiotropy and monotropy can be considered, logically and without undue hypotheses, from the same point of view. It is also held by the author that the theory of allotropy (*loc. cit.*) offers the first rational explanation of the fact that liquids, which are but little associated, separate monotropic forms, whilst liquids which are more strongly associated can separate enantiomorphic forms. The author states that the assumption of Tammann, that monotropic and enantiomorphic modifications are differently constituted, is contrary to experimental facts and theoretical conclusions. The author concludes by showing that the Tammann theory is based on a misunderstanding, and he shows that all the known facts are in agreement with his theory of allotropy. J. F. S.

New Method for the Preparation of Colloidal Solutions. A. PIERONI (*Gazzetta*, 1913, 43, i, 197—200).—[With E. TONNIONI].—When a solution of silver nitrate in dry pyridine (3.5778 grams in 50 c.c.) is treated with half its volume of a solution of pyrogallol in dry pyridine (1.1424 grams in 50 c.c.), a slightly yellow solution is obtained, which on dilution with water yields colloidal silver solutions. These appear grey by reflected light, and from yellow to orange and finally violet by transmitted light, according to the concentration. Solutions containing 0.05 gram of silver per 100 c.c. of liquid are fairly stable, and by centrifugalisation the greater part of the colloid can be separated from them. When tannic acid is used instead of pyrogallol the result is similar, but the maximum stable concentration amounts to 0.064 gram per 100 c.c. of liquid. Analogous results are obtained with solutions of copper sulphate. In these cases the separation of the colloid is caused by hydrolytic action, but many substances can be prepared in colloidal solution without the intervention of water. In this way colloidal solutions of silver sulphide and of mercury sulphide are produced on mixing pyridine solutions of hydrogen sulphide with silver nitrate or mercuric acetate, whilst if silver acetate is taken a pyridine solution of colloidal silver is obtained. R. V. S.

Kolloid-Chemical Studies of Protoplasm. WILLY REHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 113—124).—A summary of



recent work on protoplasm and the protoplasmic membrane from the colloido-chemical standpoint. A bibliography is appended.

H. M. I).

**A Fundamental Law of Dispersoidology.** PETR P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 124—127).—According to the author's generalisation, every substance tends to change in that direction which is accompanied by a diminution in its free surface energy. It is pointed out that this is a special case of the law according to which any system tends to change in such a way that its free energy diminishes, and that, as such, it is of particular importance in the case of highly disperse systems in which the surface energy is probably the essential factor concerned. A number of changes, in which the law is supposed to operate, are cited. A case in point is presented by the transformation of a solid substance into an unstable, crystalline modification, or into a liquid, when the size of the particles is sufficiently reduced. The conversion of grey, metallic selenium into the red modification furnishes an example of this type of change, and the red and yellow modifications of mercuric oxide are supposed to be similarly related. The greater facility with which water is set free from hydrated crystalline substances when their degree of dispersity is sufficiently increased, is also supposed to be due to the operation of the surface energy law. Since ordinary aqueous solutions represent the limiting condition of a series of systems of continuously increasing dispersity, it seems probable that such solutions cannot contain chemically stable hydrates such as are formed in the crystalline condition. Ionisation of electrolytes is also supposed to be a consequence of the operation of the law, because the formation of an electrical double layer at the surface of the ion will result in the diminution of the free surface energy. H. M. I).

**Regularities in the Hygroscopy of Chemical Compounds.** C. REICHARD (*Pharm. Zentr.-bl.*, 1913, 54, 287—290).—After a review of the compounds which are hygroscopic in character, the author draws the conclusion that, at present, just as many reasons can be adduced against, as for, any scheme of classification. T. S. P.

**Thermodynamic Functions of Mixtures with Reacting Components.** PETRUS H. J. HOENEN (*Zeitsch. physikal. Chem.*, 1913, 82, 695—742).—A theoretical mathematical paper in which the conditions for chemical equilibrium in the gaseous and liquid states are deduced from the second law of thermodynamics; the conditions arrived at are confirmed as far as the liquid state is concerned by other methods. The three thermodynamic functions  $\eta$ ,  $\psi$ , and  $\chi$  are defined, and their properties are considered. It is shown that they embrace systems in which there is no chemical equilibrium. The theory is extended to systems of mixtures of any composition, and it is shown in this connexion that the functions for the equilibrium of such a system are identical with the usual thermodynamic functions. The method of determining equilibria in

heterogeneous systems, by means of the new functions, is indicated, and the conditions for the existence of an ideal liquid are put forward.

J. F. S.

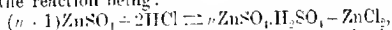
**Chemical Equilibria in Gaseous Systems.** UGO GRASSI (*Nuovo Cim.*, 1913, [vi], 5, i, 85—96).—Two determinations of the constant of the reaction  $\text{COMe}_2 + \text{H}_2 \rightleftharpoons \text{CHMe}_2\text{OH}$  at  $182^\circ$  and 76 cm. pressure gave for the reaction constant the values  $1.48 \times 10^{-2}$  and  $1.45 \times 10^{-2}$ , whilst a third experiment at  $182^\circ$  and 109 cm. pressure gave  $1.45 \times 10^{-2}$ . In these cases acetone and hydrogen were taken; in an experiment starting with the alcohol and hydrogen at  $182^\circ$  and 76 cm. pressure, the value of the constant was  $1.40 \times 10^{-2}$ . The experiments were conducted by leading purified electrolytic hydrogen through the organic substance contained in a weighed vessel kept in a thermostat. By altering the temperature of the thermostat, various mixtures of hydrogen with the vapour of the substance could be obtained. The mixture then passed through a copper tube, 180 cm. long, containing porous earth coated with reduced copper. The product of the reaction was retained in a condenser, and the excess of hydrogen escaping caught and measured. The apparatus was gas-tight, and its contents were kept at a known, constant pressure. The hydrogen was obtained by electrolysis in a cell comprising a nickel anode immersed in 25% sodium hydroxide in a porous pot; this pot in turn was placed in a second porous vessel containing a saturated solution of sodium sulphate, whilst outside this was an acid solution of copper sulphate containing a copper plate as anode.

R. V. S.

**Chemical Reactions in Strongly Compressed Gases.** EMIL BRINER (*Zeitsch. Elektrochem.*, 1913, 19, 301).—An answer to Trautz's criticism (*ibid.*, 150) of the paper of Briner and Wroczynski (*A.*, 1911, ii, 705).

J. F. S.

**Chemical Equilibrium in the Action of Hydrogen Chloride Gas on Zinc Sulphate.** CAMILLE MATIGSON (*Compt. rend.*, 1913, 156, 788—791).—A study of the system zinc sulphate-hydrogen chloride, the reaction being:



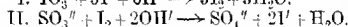
the dissociation pressure (387.6 mm.) being determined at  $0^\circ$ , has given the temperature of dissociation ( $12.3^\circ$ ) and the heat of formation (1.36 cal.) of the acid sulphate  $\text{ZnSO}_4 \cdot \text{H}_2\text{SO}_4$ . This crystalline acid sulphate completely decomposes zinc chloride at the ordinary temperature.

W. G.

**Landolt's Reaction as an Example for the Demonstration of the Foundations of Chemical Kinetics.** ALFRED TUEL (*Chem. Zentr.*, 1912, ii, 2017—2018; from *Sitzungsber. Ges. Ford. Naturwiss. Marburg*, 1912, 2, 11—35).—The influence of temperature, concentration, and catalysts on the fine-reaction, oxidation of sulphurous acid by iodic acid, is described. An increase in the concentration of the iodic acid by five times makes the reaction

nineteen times as fast, and if the concentration of both reagents is increased by five, the speed becomes fifty-three times greater. The reaction becomes slower on cooling, but heating above  $30^{\circ}$  should be avoided. Acids accelerate the reaction, and the acceleration increases with the concentration of the catalyst. Hydriodic acid has the greatest effect, and the strong mineral acids arrange themselves in order of their strengths. Neutral iodides also accelerate the reaction.

In order to incorporate the catalytic influence of acids and iodides with the theory of reactions in steps, the following equation are given:



According to this scheme, the sulphurous acid only reacts with free iodine, and the latter only appears when the former is completely oxidised. The second step is incomparably faster than the first. The scheme is supported by the fact that analogous reactions with oxidising agents which do not give up oxygen, for example the oxidation of iodine ions by persulphate ions in presence of sulphurous acid, are uninfluenced by free acids.

The oxidation of sulphurous acid by ferric salts is considerably accelerated by iodides, but the influence of acids is not so simple as in Landolt's reaction, since the anion also plays a part. The addition of nitric acid sets back the ionisation of the sulphurous acid, and the reaction is slower.

The catalytic influence of iodides on some oxidations is seen in the reaction between ferric salts and stannous salts and in the reduction of arsenic acid by hydrogen sulphide, for the addition of potassium iodide causes remarkable acceleration in each case.

J. C. W.

**The Nature of the Time Reaction between Carbonic Acid and Bases.** ALFRED THIEL (*Ber.*, 1913, 46, 867—874).—In a former paper (this vol. ii, 199) the author had no hesitation in subscribing to the explanation of the slow reaction between carbonic acid and bases (compare also this vol. ii, 198) as being due to the slow hydration of the carbonic acid, since ionic reactions, such as occurs in the neutralisation of an acid by a base, are practically instantaneous. If this explanation is correct, the time of neutralisation should be independent of the base when equivalent solutions are used. This is found to be the case when solutions of sodium hydroxide, either as such or containing equivalent quantities of strontium or barium chloride, and of barium hydroxide are used. In the case of a solution of sodium hydroxide and calcium chloride, the time of neutralisation is somewhat longer, the reason for this not being quite clear at present. With solutions of sodium hydroxide containing the equivalent amount of ammonium chloride, the times of neutralisation are considerably increased. The last fact cannot be due to a time reaction depending on the ammonium or ammonium hydroxide, since ammonia does not give a time reaction with any other acid. The author therefore draws the conclusion

that the rate of hydration of the carbon dioxide is not the deciding factor in the velocity of neutralisation, and puts forward the suggestion that the velocity depends on that of the reaction:  $\text{CO}_2 + \text{OH}' \rightarrow \text{HCO}_3'$ . If it is further assumed that this reaction has a greater velocity than that of the hydration of the carbon dioxide, it would follow that if gradually increasing quantities of sodium hydroxide, or of sodium hydroxide and ammonium chloride, are added to successive and equal volumes of a solution of carbon dioxide, the rate of neutralisation should be practically instantaneous as long as the amount of alkali added does not exceed that necessary to neutralise the carbonic acid already present in solution, since this would be an ionic reaction. As soon as this quantity of alkali is exceeded, the reaction should begin to slow down, that is, there should be a sudden break in the curve showing the relation between volume of alkali used and time of neutralisation. Moreover, this break in the curve should occur at the same place, no matter whether sodium hydroxide or sodium hydroxide plus ammonium chloride be used. The experimental results agree with these deductions, and from them the author calculates that only about 2% of the total carbon dioxide present in solution exists as carbonic acid, from which it follows that the true dissociation constant of carbonic acid is approximately  $2 \times 10^{-5}$ , that is, carbonic acid is about as strong as acetic acid.

The behaviour of a solution of carbon dioxide is thus analogous to that of an aqueous solution of a  $\gamma$ -lactone, and by experiments with  $\gamma$ -valerolactone and sodium hydroxide the author shows that the boiling solution contains about 7% of corresponding acid; after this amount of acid has been neutralised instantaneously by the sodium hydroxide, the reaction between the lactone and the alkali is a time one.

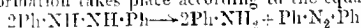
Neutral salts retard, rather than accelerate, the reaction between an aqueous solution of carbon dioxide and bases. T. S. P.

**Velocity of Formation of Precipitates.** ALEXANDER FINDLAY (*Zeitsch. physikal. Chem.*, 1913, **82**, 743). The author in reference to the paper of Jablezynski (this vol., ii, 203) calls attention to experiments of his own (A., 1900, ii, 716), in which he obtained results similar to those of Jablezynski. J. F. S.

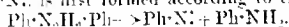
**Hydrolysis and Alcoholysis of Amides.** SULO KILPI (*Chem. Zentr.*, 1913, i, 603; from *Suomalaisen Tiedekatemian Toimituksia*, 1912, 4, iii, No. 10, 3—30. Compare A., 1912, ii, 748).—The titrimetric method for estimating the ammonium salts produced by the hydrolysis of alkyloxy-amides has been extended to cases in which the reaction takes place in an aqueous-alcoholic medium. Experiments with acetamide and propionamide showed that the reactivity of the amide may be represented by the total velocity  $k$  of the hydrolysis and alcoholysis, and in solutions containing less than 50% of alcohol this value is found to coincide with the velocity of hydrolysis  $k_1$ . J. C. W.

**The Simultaneous Oxidation of Quinol and [Sodium] Sulphite by means of Atmospheric Oxygen.** JOHANNES PINNOW (*Zeitsch. Elektrochem.*, 1913, 19, 262—268. Compare A., 1912, i, 849; Schilov and Fedotov, A., 1912, i, 966).—The authors have investigated the atmospheric oxidation of quinol and sodium sulphite mixtures, together with the influence of cupric ions on the rate of oxidation of the mixture by atmospheric oxygen. It is shown that a small quantity of sodium quinoldisulphonate acts as an anti-catalyst, protecting the sulphide from oxidation by atmospheric oxygen, and that quinol disulphonate and glycerol act in the same way, and strengthen the action the one of the other. The presence of cupric ions increases the simultaneous oxidation, and at the same time changes the relation in which the two substances are oxidised in the sense that the quinol is used up more rapidly than the sulphite. The presence of the quinoldisulphonate retards the oxidation of the quinol sulphite mixture even in the presence of cupric ions, but it has no effect on the changed oxidation relationship brought about by the cupric ions. Not only the velocity of oxidation, but also the ratio in which the two substances are oxidised, are dependent on the hydroxyl ion concentration. The action of old quinol-sulphite mixture is due, not to the presence of sulphite in a complex, but rather to the presence of sodium quinolmonosulphonate. J. F. S.

**The Transformation of Hydrazobenzene into Azobenzene and Aniline: A Reaction of the First Order.** JULIUS STIEGLIZ and GEORGE O. CREME, JUN. (*Ber.*, 1913, 46, 911—929). When an alcoholic solution of hydrazobenzene is heated in a sealed tube at 130°, transformation takes place according to the equation:



(Biehringer and Busch, A., 1903, i, 296). If this is an inter-molecular reaction, as supposed by Wieland (A., 1912, i, 902), it should be of the second order. According to the theory of Stiegliz (A., 1903, i, 235), however, it is probable that in such reactions phenylimide,  $\text{Ph}\cdot\text{N}=\text{N}\cdot\text{Ph}$ , is first formed according to the equation:



This reaction takes place slowly, and is followed by the instantaneous reaction:  $2\text{Ph}\cdot\text{N}=\text{N}\cdot\text{Ph} \rightarrow \text{Ph}\cdot\text{N}_2\cdot\text{Ph}$ . The total reaction should therefore be one of the first order, as is found to be the case experimentally.

The velocity measurements were carried out at 140.3°, the alcoholic solutions being sealed up in glass tubes under a pressure of about 20 mm. The course of the reaction was followed by adding the contents of the tubes to excess of iodine solution, and titrating the excess with thiosulphate. The velocity constant has a mean value of 4.00156, and is independent of the dilution. When the reaction is about two-thirds complete there is a tendency for the constants to fall.

T. S. P.

**Surface Combustion.** WILLIAM A. BONE (*Ber.*, 1913, 46, 968—969).—A correction with respect to the author's reference to Nernst's theory of surface catalysis in his lecture to the German Chemical Society (this vol. ii, 204).

T. S. P.

**Catalytic Oxidation at High Temperatures.** SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 286—288).—Air saturated with methyl alcohol vapour was passed through heated tubes containing aluminium turnings, reduced nickel or cobalt, manganese, or platinum, copper, silver, or gold on asbestos, the temperature and the duration of heating being varied in different experiments. With cobalt, nickel, aluminium, manganese, and platinum the maximum yields of formaldehyde were small, but with copper, 43–47% was obtained, with silver 64–66%, with gold 71%, and with silver and copper together, 84%.

The results obtained with gold, copper, and silver indicate that the maximum catalytic activity must therefore be attributed to the metal with intermediate atomic weight, just as is the case with catalytic reduction, where palladium is the most effective metal.

It appears also that, in the catalytic oxidation of methyl alcohol, occluded oxygen plays a part similar to that of hydrogen occluded by the platinum metals in catalytic reduction, and that intermediate labile oxides are formed, so that atomic oxygen takes part in the change.

T. H. P.

**Catalytic Studies. III. Catalytic Deviation of a Reaction.** EMIL ABEL and G. BAUM (*Monatsh.*, 1913, 34, 425—515).—The principal results may be summarised as follows: In the presence of molybdic acid the reaction between hydrogen peroxide and sodium tetrathionate in (acetic) acid solution gives not only tetrathionate, which is the ordinary product of reaction according to the equation (1)  $\text{H}_2\text{O}_2 + 2\text{S}_4\text{O}_6^{2-} + 2\text{H}^+ \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{H}_2\text{O}$  (Abel, A., 1908, ii, 26), but also sulphate, according to the reaction (2)  $4\text{H}_2\text{O}_2 + \text{S}_4\text{O}_6^{2-} \rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+ + 3\text{H}_2\text{O}$ . The relative proportions in which these two reactions take place, when molybdic acid is present only in traces of the order of  $10^{-5}$  mol. of  $\text{MoO}_3$  per litre, varies with the conditions of experiment between 1:1 and 1:8.

The tetrathionate reaction (1) is not influenced by the presence of molybdic acid: the sulphate reaction (2) does not proceed by way of tetrathionate, so that the course of the reaction is actually deviated by the catalytic action of the molybdic acid.

The velocity of the sulphate reaction (2) is independent of the concentration of the hydrogen peroxide, but proportional to the concentration both of the tetrathionate and of the molybdic acid; hydriions have an accelerating effect, but the reaction also proceeds in their absence. The velocity equation is

$$-d[\text{H}_2\text{O}_2]:dt = 1500[\text{MoO}_3][\text{Na}_2\text{S}_4\text{O}_6]$$

at 25°, when  $[\text{H}^+] = 0$ ,  $t$  is expressed in minutes, and the concentrations in gram-equivalents, that is,  $(\text{H}_2\text{O}_2/2)$ ,  $(\text{Na}_2\text{S}_4\text{O}_6)$ , and  $(\text{MoO}_3)$  per litre.

The total velocity of reaction is expressed, at 25°, by the two simultaneous differential equations:

$$dx/dt = 1.53[(\text{H}_2\text{O}_2) - x - y] \{ (\text{Na}_2\text{S}_4\text{O}_6) - x - y/8 \}$$

and  $dy/dt = 1500[\text{MoO}_3][(\text{Na}_2\text{S}_4\text{O}_6) - x - y/8]$ , where the quantities in round brackets give the concentrations at the commencement of

the reaction, and  $x$  and  $y$  are the concentrations at the time  $t$  of the tetrathionate and sulphate respectively formed, and expressed in the appropriate units  $\{x = (S_4O_6^{2-})/2 \text{ and } y = (SO_4^{2-})/4\}$ .

The mechanism of the reaction leading to the production of sulphate consists in the formation, with unmeasurable velocity, of a permolybdic acid, which then oxidises the thiosulphate to sulphate. This latter reaction takes place in stages, but the stage which regulates the velocity is bimolecular.

The analytical methods used in this investigation were based on previous work of Abel's (A., 1912, ii, 486).

The authors call attention to the analogy existing between this catalytic deviation of an inorganic reaction and the selective course pursued by ferment and enzyme reactions.

T. S. P.

**A Condenser in One Piece for the Kjeldahl Estimation of Nitrogen.** ERNST PESCHKE (*Zeitsch. angew. Chem.*, 1913, 26, 176).—The author describes a piece of apparatus in which the trap to check spray, the condenser, and the tube leading into the receiving flask form one piece of glass. The tube leading to the condenser is sloped downwards throughout its length towards the distilling flask, so that any alkali dissolved from the hot glass by the condensed steam is prevented from passing down the condenser.

D. F. T.

## Inorganic Chemistry.

**The Acidity of Water and of Hydrogen Peroxide and the Uniformity of Compounds.** Preliminary Note. JOACHIM SPERBER (*Chem. Zentr.*, 1913, i, 502; from *Schweiz. Woch. Chem. Pharm.*, 1912, 50, 741).—Since Merck's acid-free "perhydrol" liberates the acid from sodium silicate, borax, sodium metaphosphate, and potassium ferro- and ferri-cyanides, it is regarded as an acid, and since water sets free hydrogen peroxide from peroxides, it also is classed as an acid, "water acid." Oxides therefore become "aquates" and peroxides "hyperaquates," and hydrogen is assumed to be a metal.

J. C. W.

**Application of Hot Centrifugation to the Estimation of the Composition of Hydrates with Low Water Content.** PETR KUNETZOV (*Chem. Zentr.*, 1913, i, 765; from *Izvestia Don. Polytech. Inst. Novotscherkask*, 1912, 1, ii, 389—398).—For the isolation of lower hydrates which are stable at higher temperatures it is recommended to surround the centrifuge with a mantle through which hot water may flow. By this means the hydrates,  $MnBr_2 \cdot 2H_2O$ ,  $CaBr_2 \cdot 2H_2O$ , and  $NiBr_2 \cdot 2H_2O$ , have been obtained.

J. C. W.

**Weight of a Normal Litre of Gaseous Chlorine and Silicon Tetrafluoride. Determination of the Atomic Weights of Chlorine and Fluorine.** ADRIEN JAQUERON and MELCON TOURPATIAN (*J. Chim. phys.*, 1913, **11**, 3—28. Compare A., 1911, ii, 189).—The authors' displacement method of measuring gaseous densities, which has the advantage that no mercury pump or greased stop-cocks are necessary, has been applied to the corrosive gases chlorine and silicon tetrafluoride.

The weight of a normal litre of chlorine, liberated from hydrochloric acid by manganese dioxide or potassium permanganate, or by heating auric chloride, was found to be 3.214 grams. The values obtained by the displacement method and by means of a special form of Dumas bulb are in fair agreement.

Silicon tetrafluoride was prepared by the action of concentrated sulphuric acid on a mixture of calcium fluoride and quartz sand for the displacement experiments, and by heating barium silicofluoride for the Dumas bulb experiments, which gave a slightly higher value. The weight of a normal litre was found to be 4.693 grams.

When silicon tetrafluoride is passed over glass-wool at red heat to remove hydrogen fluoride according to Moissan's procedure, a subfluoride is apparently formed, since the normal litre weight increases to 4.820 grams.

In view of the uncertainty of the compressibility data used in the reduction of their experimental values, the authors' results cannot be employed at present to calculate the atomic weights of chlorine and fluorine.

R. J. C.

**Preparation of Perchloric Acid.** FRANK C. MATHERS (*Chem. Zeit.*, 1913, **37**, 363).—One hundred grams of potassium perchlorate are distilled with 60 c.c. of concentrated sulphuric acid under a pressure of 10 cm.; meanwhile, water-vapour should be led into the distillation flask in such quantity that no crystals ( $\text{HClO}_4 \cdot \text{H}_2\text{O}$ ) collect in the condenser. Only very little vapour is necessary, but an excess does not matter, as it only causes slight spitting and prolongs the distillation. The neck of the distilling flask should be lengthened in order to prevent the rubber stopper being attacked. Two hundred grams of potassium perchlorate are the most which can be used in a litre flask. The concentration of perchloric acid obtained varies from 88 to 98%.

If sodium perchlorate is used, 20 grams are treated with 30 c.c. of concentrated hydrochloric acid. The sodium chloride formed is insoluble, and the hydrochloric acid in the filtrate from it is driven off at 135°, whereby a 95% perchloric acid is obtained (compare Mathers, A., 1909, ii, 287).

T. S. P.

**The Finding of Iodine in the Waters of the Dead Sea, and the Detection of Iodine in Concentrated Solutions Rich in Magnesium Salts.** HEINRICH FRESSENIUS (*Verh. Ges. deut. Naturforsch. Verste.*, 1913, 118—120).—The water, which was



collected in the latter half of 1909, had D<sup>15</sup> 1.1555 and the following composition, expressed in terms of grams per kilogram of water:

K.	Na.	Ca.	Mg.	Fe (ons).	Cl.	Br.	I.	SO <sub>4</sub> .	HClO <sub>2</sub> .
4.411	25.88	7.892	23.21	0.007586	124.1	2.124	0.000247	0.7319	0.0027

Magnesium chloride is present in by far the largest amount, then follow, in order, sodium chloride, calcium chloride, potassium chloride, sodium bromide. Sulphates are present to only a slight extent, hydrogen carbonates to a very slight extent, and iodides in traces. The presence of iodides has not previously been detected, probably owing to the fact that when the water is evaporated, hydrolysis of the magnesium iodide occurs, and the hydrogen iodide formed is driven off; this action takes place with the bromide also. In order to retain all the bromine and iodine in the solution during evaporation, it is necessary first to decompose all the magnesium compounds present with milk of lime.

The following method was used for the detection and estimation of bromine and iodine in such waters: 1090 grams of the water were diluted, heated to boiling, and then precipitated with an excess of milk of lime. After collecting the precipitate, the filtrate was evaporated, the residue powdered, and extracted four times with 96% alcohol. To the alcoholic extract were added a few drops of concentrated potassium hydroxide solution, the alcohol distilled off, and the residue heated until it glowed slightly, after which it was dissolved in water and the iodine liberated with nitrous acid. The iodine was extracted with carbon disulphide and estimated, after which the bromine (and some chlorine) was precipitated with silver nitrate and estimated by determining the loss in weight occurring on heating in a stream of chlorine. T. S. P.

**Behaviour of Iodine towards Sulphur, Selenium, and Tellurium.** ERNST BECKMANN and RUDOLF HANSLAN (*Zeitsch. anorg. Chem.*, 1912, 80, 221-234).—The molecular weight of selenium in iodine has been found (Olivari, A., 1909, ii, 39) to be Se<sub>2</sub> instead of Se<sub>8</sub>, whilst there is no indication of the presence of a compound (Pellini and Pedrina, A., 1908, ii, 833). The low molecular weight is confirmed, and is almost the same at 181° as at 101°. Sulphur gives values falling little below Se<sub>2</sub>.

Anthraquinone (cryoscopic constant 148) gives Se<sub>2</sub> and Se<sub>4</sub>, whilst diphenyl (ebullioscopic constant 59.3) gives similar values. It is therefore a specific influence of the iodine, and not of high temperature, that causes the dissociation of the selenium molecule.

Tellurium reacts with iodine, and the cryoscopic and ebullioscopic results indicate a large proportion of single atoms. Red phosphorus in iodine gives P<sub>4</sub>, a chemical reaction taking place. C. H. D.

**Analysis and Preparation of Fuming Sulphuric Acid of Given Strength.** JOSÉ PRATS AYMERICH (*Anal. Fis. Quim.*, 1913, 11, 118-136).—Formulae and tables for use in the preparation of acid of a desired strength. G. D. L.

**Selenium Oxybromide.** R. TH. GLAUSER (*Zeitsch. anorg. Chem.*, 1913, **80**, 277—279).—When selenium oxychloride is distilled with sodium bromide, a dark red liquid is obtained, which solidifies, forming yellow needles, and has the composition  $\text{SeOBr}_2$ . The same compound has been obtained from selenium tetrabromide and selenium dioxide. The crystals melt between  $30^\circ$  and  $40^\circ$ , dissolve in sulphuric acid, and may be largely recovered after treatment with small quantities of water. (C. H. D.)

**The Atomic Weight of Tellurium.** PETR KUSMERZOV (*Chem. Zentr.*, 1913, i, 772—773; from *Izvesta Don. Polytech. Inst. Novosibirsk*, 1912, **1**, ii, 380—387).—When the differences between the atomic weights of the elements in the eleven periods are tabulated, they show a regular rise and fall within the separate groups. The negative difference between iodine and tellurium is in accordance with the other differences in the sixth group.

J. C. W.

**The Oxidation of Nitrogen and Active Nitrogen.** FRANZ RUSS (*Osterr. Chem. Zeit.*, 1912, **15**, 316).—A discussion of the thermal and electrical principles which may account for the formation of active nitrogen (compare Ehrlich and Russ, A., 1912, ii, 41, and Stütt, A., 1911, ii, 182, 1056). (F. M. G. M.)

**The Action of Ozone on Liquid Ammonia.** WILHELM MAXCHOT (*Ber.*, 1913, **46**, 1089—1093).—When ozone ( $10\text{--}11\%$ ) is passed into liquid ammonia at  $-70^\circ$ , an orange-red colour is produced (compare A., 1908, ii, 101), which rapidly pales at  $-65^\circ$  to  $-60^\circ$ , when the current of ozone is stopped: above  $-60^\circ$  the colour practically disappears. In the presence of a few drops of water, the colour is more stable, persisting to towards  $-50^\circ$ . The addition of much water makes the colour less stable. If the ammonia is dissolved in anhydrous solvents like carbon tetrachloride, chloroform, etc., there is no formation of colour, neither do anhydrous trimethylamine and dimethylamine give rise to colour. However, the amines react similarly to ammonia (*loc. cit.*) in that, on acidifying after treatment with ozone, titanium sulphuric acid gives an intense reaction for hydrogen peroxide.

If liquid ammonia, contained in a U-tube, is cooled in liquid air, a layer of liquid ozone condensed over it, and then the U-tube allowed to warm up gradually to the temperature of the air, no explosion occurs. If the ammonia is replaced by di- or trimethylamine, explosion occurs under the same conditions.

The colours obtained with ammonia are probably due to the presence of slight traces of water, which it is difficult to exclude. They are very similar to those obtained with ozone and potassium hydroxide (*loc. cit.*), and it would seem as if, in this respect, the ammonium hydroxide formed is more similar to the alkali hydroxides than di- and trimethylammonium hydroxides. That the amines give no colour may, however, be due to the fact that at the low temperatures used the conditions are not favourable to the

formation of substituted ammonium hydroxides from the liquid amines. T. S. P.

**Tension of Metal Ammine Compounds.** WILHELM HERTZ (*Zeitsch. physikal. Chem.*, 1913, 82, 688-694).—A criticism of Ephraïm (this vol., ii, 129, 130). It is shown that Ephraïm's statement, that the ammine salts split off ammonia one molecule at a time with the formation of all the possible amines, is based on an error. The author demonstrates experimentally that only two amines of nickel bromide exist, namely, the hexammine and the diammine. J. F. S.

**The Allotropy of Phosphorus.** WALTER A. WAHL (*Chem. Zentr.*, 1913, i, 774-776; from *Öfversigt Finska Vetensk. Soc. Förhändl.*, 1911, 54, A, 9, 22 pp. Compare Jolibois, A., 1909, ii, 726; 1910, ii, 846; Cohen and Olie, A., 1909, ii, 998).—When red phosphorus is heated in a strong capillary tube, it becomes almost black at 500°, and melts at 600° to a yellow, mobile liquid. On cooling, the colour deepens to a reddish-brown until solidification occurs. Purified, molten white phosphorus does not absorb light, but in the daylight the liquid becomes yellow, and then absorbs rays of 486mμ and smaller. When a drop of white phosphorus, under water, is illuminated by a quartz mercury lamp, it immediately receives an elastic coating of red phosphorus.

From these experiments, the conclusion is drawn that molten red phosphorus is not identical with molten white phosphorus, but that at comparatively low temperatures it exists as a liquid of such high viscosity as to be vitreous. Between the two molten modifications, equilibria exist at different temperatures, but the pure molten white phosphorus is not an equilibrium mixture, since the speed of transformation into red phosphorus is extremely small below 250° in the dark. The fact that a labile substance can melt without passing into the stable form is seen in the case of benzophenone (this vol., i, 488). Above 250°, transformation proceeds apace, and the speed can be accelerated by catalysts. The colour of the red phosphorus which separates depends on the temperature, since devitrification occurs at high temperatures. Whether other modifications are produced in this process is uncertain, but Hittorf's crystallised phosphorus may be one of them. J. C. W.

**Formation of Hydrogen Phosphide from Phosphorus and Potassium Hydroxide.** E. LÖWENHARDT (*Zeitsch. physikal. Chem.*, 1912, 25, 368).—The author describes a simple method for preparing hydrogen phosphide without the presence of hydrogen or other inert gases.

The generating flask (a 125 c.c. Erlenmeyer) is filled to within 4 c.c. of the stopper with potassium hydroxide solution, and after adding the phosphorus gently warmed until the reaction starts; the delivery tube consists of a wide glass tube with a not too narrow outlet, and is dipped into warm water. As the action proceeds, the delivery tube becomes filled with white fumes of phosphoric oxide, and only a very slight or no explosion takes place. F. M. G. M.

**The Action of Sulphur Trioxide on Silicon Tetrachloride.** CHARLES R. SANGER and EMILE R. RIEGEL (*Zeitsch. anorg. Chem.*, 1913, **80**, 252—276. Compare A., 1912, ii, 752).—Molten sulphur trioxide and silicon tetrachloride mix at first without reacting, but the reaction,  $2\text{SiCl}_4 + 2\text{SO}_3 = \text{Si}_2\text{OCl}_6 + \text{S}_2\text{O}_3\text{Cl}_2$ , sets in very slowly in the cold, more rapidly at  $50^\circ$ , being then complete in six to ten hours. In presence of a large excess of sulphur trioxide, the further reaction occurs:  $\text{Si}_2\text{OCl}_6 + 6\text{SO}_3 = 2\text{SiO}_2 + 3\text{S}_2\text{O}_3\text{Cl}_2$ . Silicophosgen is not obtained. The two compounds,  $\text{Si}_2\text{OCl}_6$  and  $\text{S}_2\text{O}_3\text{Cl}_2$ , appear to form a molecular compound on warming, which solidifies at  $-78^\circ$ , whilst a simple mixture of the two substances solidifies at about  $-38^\circ$ . In presence of water, chlorosulphonic acid, silica, and unaltered silicon tetrachloride are obtained, but not silicophosgen.

C. H. D.

**The Alteration which takes place in Potassium Polysulphide.** HENRI PECKER (*J. Pharm. Chim.*, 1913, [vii], 7, 313—315).—Analysis of potassium polysulphide, which had been kept since 1906, showed that it had been completely decomposed; no trace of sulphide was present, the sulphur being either in the free state or as thiosulphate or sulphate. Only a trace of carbonate was present, so that the decomposition was not due to carbonation. The polysulphides disappear with the formation, chiefly, of thiosulphate, the oxidation being brought about by moist air.

T. S. P.

**The Anhydrous Protosulphides of the Alkali Metals.** ERIENNE RENGADE and N. COSTEAU (*Compt. rend.*, 1913, **156**, 791—793).—The authors have prepared the sulphides of sodium, potassium, rubidium, and cesium in a pure anhydrous form by the direct action of sulphur vapour on an excess of the alkali metal at a temperature between  $200^\circ$  and  $300^\circ$ . On distilling off the excess of the metal, the sulphide crystallises out. They are all white, microcrystalline powders at the ordinary temperature, turning yellow as the temperature rises. The sulphides are less coloured and less soluble in their metals than the corresponding oxides, but the solubility increases with rise in atomic weight of the metal. They are more stable than the oxides, being unaltered by light, and are not decomposed by heat except at very high temperatures, when they give persulphides and vapours of the metals.

W. G.

**Acid Sulphates. VII. Acid Sulphates and Pyrosulphates of Sodium, Potassium, and Ammonium.** JOUANES D'ANS (*Zeitsch. anorg. Chem.*, 1913, **80**, 235—245).—The solubility isotherms of the three systems  $\text{SO}_3\text{--H}_2\text{O}$ -alkali sulphate have been determined at  $25^\circ$ , and the following solid phases have been observed in contact with the solution:  $\text{NaHSO}_4$ ;  $\text{NaH}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ;  $\text{Na}_2\text{SO}_4 \cdot 4.5\text{H}_2\text{SO}_4$ ;  $\text{NaHS}_2\text{O}_7$ ;  $\text{KHSO}_4$ ;  $\text{KH}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ;  $\text{KH}_2(\text{SO}_4)_2$ ;  $\text{KHS}_2\text{O}_7$ ;  $(\text{NH}_4)_2\text{HSO}_4$ ;  $(\text{NH}_4)_2\text{H}_2(\text{SO}_4)_2$ ;  $(\text{NH}_4)_2\text{HS}_2\text{O}_7$ . The data and triangular diagrams for the three ternary systems  $\text{SO}_3\text{--H}_2\text{O}$ -alkali oxide at  $25^\circ$  are also given.

C. H. D.

**A New Form of Potassium Dichromate.** ALEXIS DEFORGE (*Compt. rend.*, 1913, 156, 1022—1024. Compare Wyruboff, *Bull. Soc. franç. Min.*, 1890, 13, 309).—By the addition of a considerable excess of aluminium sulphate to a solution of potassium chromate, the latter is partly converted into potassium dichromate, with the precipitation of aluminium hydroxide, and on concentration by heat the salt separates as a mixture of triclinic and monoclinic crystals. The latter are isomorphous with rubidium and ammonium dichromates, the optical figures for the crystals of the three substances being:

$K_2Cr_2O_7$ .....	$a : b : c = 1.0167 : 1 : 1.7716$	$\beta = 91.55^\circ$
$Rb_2Cr_2O_7$ .....	$a : b : c = 1.0202 : 1 : 1.8081$	$\beta = 95.28^\circ$
$(NH_4)_2Cr_2O_7$ .....	$a : b : c = 1.0271 : 1 : 1.7465$	$\beta = 93.49^\circ$

Although they are the unstable form, the monoclinic crystals exhibit false equilibrium, and can be kept in contact with triclinic crystals in the cold without any appreciable change. They dissolve in a solution saturated with respect to triclinic crystals at  $12.5^\circ$ , whereas triclinic crystals are unaffected under the same conditions. On heating, the monoclinic crystals decrepitate, and then behave like the triclinic crystals (compare Le Bel, *A.*, 1912, ii, 49).

W. G.

**Sodium Silicate. Preparation and Recrystallisation of Sodium Silicate,  $Na_2SiO_3 \cdot 9H_2O$ .** ALBERT VESTERBERG (*Chem. Zentr.*, 1913, i, 777; from *Proc. VIII. Intern. Cong. Appl. Chem.*, 1912, 2, 235—239).—When commercial water glass solution is mixed with sodium hydroxide and alcohol, the lower layer consists of a super-saturated solution of sodium silicate, and deposits orthorhombic crystals,  $Na_2SiO_3 \cdot 9H_2O$ , m. p.  $480^\circ$  (approx.), in the course of time. The following solubilities are given; the figures refer to 100 c.c. of solution at  $17.5^\circ$ : In 0.5N-sodium hydroxide, 25.56 grams, D 1.129; in 0.5N-sodium chloride, 33.83 grams, D 1.150; in saturated brine containing 27.91 grams sodium chloride, 20.61 grams per 100 c.c. of solution. When kept over 50% potassium hydroxide or concentrated sulphuric acid, the crystals change into the *hydrate*,  $Na_2SiO_3 \cdot 3H_2O$ , which soon absorbs water from sodium hydroxide of D 1.26 to form the *hydrate*,  $Na_2SiO_3 \cdot 6H_2O$ . The ordinary hydrate speedily loses  $6H_2O$  at  $100^\circ$ , but it must be strongly heated to remove the last traces of water. Anhydrous sodium silicate has m. p.  $1007^\circ$ . J. C. W.

**Hydrates of Calcium Oxide and their Molecular Compounds. II. Supersaturated Solutions of Hydrated Calcium Oxide.** FEDOR FEDOROVITSH SELIVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 252—257. Compare this vol., ii, 211).—Supersaturated solutions prepared by freezing solutions of hydrated calcium oxide under various conditions were found to contain 0.260–0.284 gram of CaO per 100 c.c. This concentration is in agreement with that obtained in Guthrie's first experiment, but the author was not able to prepare a solution containing 0.29 gram of CaO per 100 c.c., as indicated by Guthrie's second experiment (*A.*, 1879, ii, 128). The

limiting concentration attained by freezing is hence 1 mol. CaO to 1184 mols.  $\text{H}_2\text{O}$ .

These supersaturated solutions are extremely sensitive to heat, and readily deposit crystals of the hydroxide,  $\text{Ca}(\text{OH})_2$ , at the ordinary temperature. Even if the cold supersaturated solution is poured into a glass vessel at the ordinary temperature, the whole of the interior of the vessel becomes coated with the crystals. The formation of the crystals may, however, be retarded by keeping the solution vigorously agitated.

Presence of either of the crystalline hydrates,  $2\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$  (see following abstract), or of the amorphous hydroxide,  $\text{Ca}(\text{OH})_2$ , produced no change in the supersaturated solutions, the excess of hydrate in the latter not being deposited. The crystalline hydrates are precipitated more readily on a glass vessel than on similar crystals.

The behaviour of the supersaturated solutions is similar to that shown by supersaturated gypsum solution (compare Potilitzin, A., 1894, ii, 39, 44), and it may be that supersaturated solutions of lime contain a stable hydrate, which is converted only with difficulty into hydrates of the compositions,  $\text{Ca}(\text{OH})_2$  and  $2\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ . Such explanation is not, however, in good agreement with the properties of the known hydrates of lime, the sesquihydrate being highly unstable and easily transformable into the monohydrate; similar instability would be expected in hydrates containing more water than the sesquihydrate.

T. H. P.

**Hydrates of Calcium Oxide and their Molecular Compounds. III. Crystalline Hydrates.** FEDOR F. SELIVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 257-266. Compare preceding abstract).—The monohydrate of calcium oxide,  $\text{Ca}(\text{OH})_2$ , may be obtained in hexagonal plates or prisms by heating supersaturated solutions of lime or by evaporating aqueous lime solutions under diminished pressure at 28–30°. This crystalline hydrate is less soluble in water and in dilute sugar solutions than the amorphous hydrate having the same composition, the two hydrates hence being assumed to be in different physical conditions. Amorphous substances are regarded as highly supercooled liquids, the molecules of which would pass into solution less readily than those of crystalline substances. It may be, also, that the molecular weights of the two hydrates are different; indeed, the amorphous form cannot be transformed into the crystalline form either by heating with water or by prolonged storage over water.

The cryohydrate of lime gives, on solidification, absolutely transparent ice, but the solution formed when this ice melts deposits elongated hexagonal plates or small, rhombic plates of the sesquihydrate,  $2\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , which is very unstable, and decomposes when only slightly heated, giving the amorphous hydrate; it is less soluble in water than the monohydrate.

T. H. P.

**The System Lime. Phosphoric Oxide and Silica.** OTTO NIELSEN (*Ferrum*, 1913, 10, 97–112).—Tricalcium phosphate,

$\text{Ca}_3(\text{PO}_4)_2$ , has m. p.  $1550^\circ$ , and is not reduced by carbon monoxide. Carbon begins to reduce it at  $1400^\circ$ . It is not decomposed by silica in a neutral atmosphere, but a chemical combination occurs at  $1150^\circ$ , and the product is completely reducible by carbon. This compound has the composition  $3\text{CaO} \cdot 3\text{SiO}_2 \cdot \text{P}_2\text{O}_5$ , a strong maximum being found on the freezing-point curve of mixtures of calcium phosphate and silicate at this composition and  $1630^\circ$ . Two compounds,  $2\text{SiO}_2 \cdot \text{P}_2\text{O}_5$  and  $3\text{SiO}_2 \cdot \text{P}_2\text{O}_5$ , have also been found, the last of which melts without decomposition in the oxy-hydrogen flame.

C. H. D.

**The Permeability of Glass for Water under the Influence of Electricity of High Tension.** FRIEDRICH MEYER (*Ber.*, 1913, 46, 1110—1115).—In contradistinction to Schützenberger (*A.*, 1890, 1358), the author cannot find the least trace of permeability of glass towards water vapour under the influence of a high tension discharge.

T. S. P.

**Ternary Alloys of Magnesium, Aluminium, and Zinc.** GEORG EGER (*Intern. Zeitsch. Metallographie*, 1913, 4, 29—128).—This complex system has been investigated fully by thermal and micrographic methods. The two compounds,  $\text{Al}_3\text{Mg}_2$  and  $\text{MgZn}_2$ , form binary solid solutions, whilst the former also forms ternary solid solutions. There appears to be a ternary compound,  $\text{Al}_3\text{Mg}_4 \cdot 3\text{MgZn}_2$ , which decomposes on melting, and forms solid solutions. The branch of the liquidus corresponding with this constituent ends in a eutectic point at  $450^\circ$ .

All the alloys are harder than aluminium, and most are brittle. All those containing free magnesium are attacked by moist air. The eutectic alloy, with Zn 93.5, Mg 3.3, Al 3.2, is tough, and takes a high polish.

C. H. D.

**Influence of Thermal Treatment on the Solidification and Transformation of Cadmium-Tin Alloys.** DOMENICO MAZZONI (*Intern. Zeitsch. Metallographie*, 1913, 4, 13—28).—The heat content of twelve alloys of tin and cadmium has been determined by comparing their rate of cooling with that of mercury under exactly the same conditions. The results obtained are in close agreement with those arrived at by Guertler (*A.*, 1912, ii, 650) from theoretical considerations. The saturation point of the  $\gamma$ -tin solid solution at the eutectic temperature is 90% Sn, whilst the maximum heat effect of the transformation at  $130^\circ$  occurs at 91.5% Sn. It is therefore unlikely that any compound is formed, and the transformation consists in the separation of cadmium from solid solution in Cd, a eutectoid alloy being formed. The solubility of cadmium in  $\beta$ -tin is about 1%. The heat of solution of cadmium in  $\gamma$ -tin is about 30 cal. per gram, or about twice the heat of fusion of cadmium. In such alloys, equilibrium is only obtained by quenching rapidly in order to obtain small crystals, and then annealing for long periods just below the eutectic or eutectoid point.

C. H. D.

**Crystallisation in the Ternary System Cadmium-Potassium-Sodium Bromides.** HERMANN BRAND (*Jahrb. Min.*, 1913, i, 9-27).—Binary mixtures of cadmium bromide (m. p. 567°) and potassium bromide (m. p. 735°), and of cadmium bromide and sodium bromide (m. p. 746°) in varying proportions were fused and the concentration-temperature diagrams given. With the former pair there are double salts,  $\text{CdBr}_2 \cdot \text{KCl}$  (orthorhombic, m. p. 354°) and  $\text{CdBr}_2 \cdot 4\text{KCl}$  (rhombohedral, m. p. 324°), and also eutectics of these together and with the simple salts. The second pair yields no double salt, but only a eutectic mixture. For the ternary system of these salts five sections of the concentration-temperature diagram are given.

L. J. S.

**Compounds of Cerium Chloride with Ammonia.** MAURICE BARRE (*Compt. rend.*, 1913, 156, 1017-1019).—Cerium chloride readily forms additive compounds with ammonia. Gaseous ammonia, when introduced into a tube containing cerium chloride at -80°, combines with the chloride with the development of heat, and there is a considerable increase in the volume of the mass. By a study of the dissociation pressures, the author has established the existence of five different compounds of cerium chloride with ammonia, and has then prepared them in the form of white powders decomposable by water. The compounds are:  $\text{CeCl}_3 \cdot 20\text{NH}_3$ ;  $\text{CeCl}_3 \cdot 13\text{NH}_3$ ;  $\text{CeCl}_3 \cdot 8\text{NH}_3$ ;  $\text{CeCl}_3 \cdot 4\text{NH}_3$ ; and  $\text{CeCl}_3 \cdot 2\text{NH}_3$ .

W. G.

**A New Double Sulphate of Cerium and Silver.** M. EMANUEL POZZI-ESCOR (*Compt. rend.*, 1913, 156, 1074).—By the addition of a warm concentrated solution of silver nitrate to a solution of ceric sulphate in warm concentrated sulphuric acid, deep orange-yellow, prismatic crystals are precipitated which, after filtering, washing, and drying in a current of air at 400°, give the bright orange-yellow double sulphate,  $10\text{Ce}(\text{SO}_4)_3 \cdot 6\text{Ag}_2\text{SO}_4$ , which slowly takes up moisture, giving crystals containing  $2\text{H}_2\text{O}$ . The anhydrous double sulphate is only sparingly soluble in cold water, but readily soluble, with decomposition, in boiling water.

W. G.

**Solubility in Water of Lead as a Couple with and as an Alloy with Other Metals.** ALBERTO SCALA (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 155-162).—The experiments deal with the solubility of lead in water in lead-zinc, lead-tin, lead-carbon, and lead-copper couples, and in various lead-tin alloys. The results indicate that the solubility is not increased in these circumstances.

R. V. S.

**The Equilibrium between Lead Chloride and Ammonium Chloride in Aqueous Solution.** (Mme.) N. DEMASSEUX (*Compt. rend.*, 1913, 156, 892-894).—A study of the equilibrium between lead chloride and ammonium chloride in aqueous solutions at three different temperatures, 17°, 50°, and 100°. Curves are given showing the ratio between the amounts of lead chloride and ammonium



chloride in solution, and the results show that the double chloride,  $\text{PbCl}_2 \cdot 2\text{NH}_4\text{Cl}$ , can only exist in aqueous solution at temperatures above  $70^\circ$ . The two branches of the curves corresponding with  $\text{PbCl}_2$  and  $2\text{PbCl}_2 \cdot \text{NH}_4\text{Cl}$  are practically in the same direction, where they cut, at the eutectic.

W. G.

**Variations of the Physical and Chemical Properties of Red Lead.** OLIVER W. BROWN and A. R. NEYS (*J. Ind. Eng. Chem.*, 1912, **4**, 867—876).—A detailed account of numerous methods employed in the manufacture of red lead, with microphotographs showing the great variety of texture exhibited by commercial specimens, if it is prepared from different sources and by different processes. The following conclusions are drawn:

Red lead may be either crystalline or amorphous.

The crystalline modification has no definite form, but the crystals retain the form of the material from which the red lead was prepared.

The sp. gr. varies from 8.32 to 9.16. The variations in sp. gr. depend on (a) the temperature at which the oxide is formed, (b) the time of heating, (c) the chemical composition, and (d) the physical nature of the starting material.

The apparent density depends mainly on the fineness of the particles of the oxide, decreasing as the fineness increases up to a certain point. The temperature most suitable for the formation of red lead varies with the starting material used; about  $425$ – $430^\circ$  is best for white lead,  $150$ – $470^\circ$  for litharge and lead sponge; and about  $450^\circ$  for converting lead hydroxide and metallic lead into red lead,  $450^\circ$  being probably the temperature at which red lead can be most economically formed from any suitable starting material. Any red lead is rapidly and completely reduced to litharge at  $525$ – $530^\circ$ .

Both "yellow" and "red" litharge are much more slowly roasted to red lead after being treated with water, showing that "air separation" of the litharge before roasting is to be preferred to "floating" in water.

F. M. G. M.

**Compound of Varying Composition in Alloys of Thallium and Bismuth.** NIKOLAI S. KURNAKOV, SERGEI F. SHEMITSCHUSHNI, and V. TARARIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 300–320).—In the case of lead-thallium alloys, the distectic point is found to correspond with variable and irrational ratios between the atomic proportions of the constituent metals (compare Kurnakov and Puschin, A., 1907, ii, 262; Lewkonja, A., 1907, ii, 261; Kurnakov and Shemitschushni, A., 1909, ii, 855). A more marked example of this phenomenon is furnished by bismuth-thallium alloys, which give three irrational melting point maxima, relating to three distinct phases.

The authors' investigation of these alloys extends to the thermal relations, the electrical conductivity and the temperature coefficient of the resistance, the hardness and the pressure of efflux, and the micro-structure.

Analysis of the melting-point diagram indicates the existence of three phases of the compositions: ( $\alpha$ ) 0—5.8 atom. % Bi; ( $\beta$ ) 5—33.0 atom. % Bi; and ( $\gamma$ ) 55—64 atom. % Bi. Not one of the three corresponding maximal melting points accords with a rational atomic ratio between the constituent metals, and, as regards the first two maxima, there is general agreement between previous authors on this point. For the third maximum the authors find 62.8 atom. % Bi, which does not differ sufficiently from the 62.5% required for the compound  $\text{Bi}_2\text{Tl}_3$  to admit of the existence of this compound being denied (compare Chikashigé, A., 1907, ii, 88), especially as the diagram for the  $\gamma$ -phase is exactly similar in form to many other curves with rational distectics.

With the curves of electrical conductivity and of temperature-coefficient of resistance at various temperatures, the maxima for the  $\gamma$ -phase correspond in all cases with one definite concentration, 64 atom. % Bi, giving irrational proportions of the two metals.

The existence of the compound  $\text{Bi}_2\text{Tl}_3$  is therefore not in accord with the experimental data, and this conclusion is confirmed by the results of (1) measurements of the pressure of efflux and of the hardness, both by Brinell's ball test and by Ludwik's method (*Baunaterialienkunde*, 1907, 12, 115, 147), and (2) micrographic examination.

The  $\gamma$ -phase cannot be regarded as conforming to any one of Roozeboom's four principal types of solid solutions. The micro-structure and the melting-point diagram show that it possesses individual properties which in other systems correspond with typical chemical compounds, but the diagrams of the various properties exhibit no Dalton or singular point. It is therefore to be considered as belonging to the class of "indefinite compounds," the existence of which was defended by Berthollet in his dispute with Prout at the beginning of last century. T. H. P.

**The Ternary System Copper-Cadmium Antimony.** ALADAR SCHLEICHTER (*Intern. Zeitsch. Metallographie*, 1913, 3, 102—126).—A considerable portion of this system has been investigated thermally and microscopically. The system  $\text{SbCu}_2$ - $\text{SbCd}$  behaves as a pseudo-binary system, with a eutectic point. The great liability of antimony-cadmium alloys to undercooling, whereby the formation of the compound  $\text{SbCd}$  is suppressed, and only  $\text{Sb}_2\text{Cd}_3$  is produced (Kurnakov and Konstantinov, A., 1908, ii, 391), is also observed in the ternary system. The compound  $\text{SbCu}_2$  does not take up cadmium in solid solution, but  $\text{SbCd}$  takes up 8 atomic % of copper. The partial ternary system  $\text{SbCu}_2$ - $\text{SbCd}$ - $\text{Sb}$  has been examined in detail, and this portion of the space-model constructed.

The system  $\text{Cu}_2\text{Cd}_3$ - $\text{Sb}_2\text{Cd}_3$  is also pseudo-binary, and it is probable that  $\text{SbCu}_2$  forms pseudo-binary systems with both  $\text{Cu}_2\text{Cd}_3$  and  $\text{Sb}_2\text{Cd}_3$ . C. H. D.

**The Changes in Dilute Mercuric Chloride Solutions.** MARCEL DELÉPINE (*Chem. Zentr.*, 1913, i, 49—50; from *Bull. Sci. Pharmacol.*, 1912, 19, 610—622).—The changes which dilute solutions

of mercuric chloride suffer under the influence of light and air are chiefly due to the hydrogen carbonates in water, and the addition of sufficient acid to decompose these substances renders the solutions stable over a prolonged period.

J. C. W.

**The Action of Hydroxyl Ions on Colloidal Clay.** PARL ROHLAND (*Biochem. Zeitsch.*, 1913, 49, 447—450).—Alkalis cause a colloidal chemical change in clays, which is associated with an increase of volume of the latter. The colloidal particles of the clay appear to undergo a coagulation, which is of reversible character. The concentration of the hydroxyl group does not undergo any change during the process, and different clays require different amounts of hydroxyl concentrations to produce the change. These amounts have not, up to the present, been correlated with the chemical composition of the clay.

S. B. S.

**The Formation of Temper-Carbon in Malleable Castings.** A. SIESSNER (*Ferrum*, 1912, 10, 41—54).—The decomposition of cementite into iron and temper-carbon by heating below 1130° is accompanied by the development of heat. The inhibiting influence of 0.05% of sulphur on the decomposition is just neutralised by the presence of 0.28% of silicon.

C. H. D.

**The Theory of Undercooled Solid Solutions and the Nature of Austenite and Martensite.** H. HANEMANN (*Zurich. Zeitsch. Metallographie*, 1913, 3, 127—141).—The effect of undercooling a solid metallic solution, followed by tempering, is not necessarily to produce the eutectoid, the formation of which was suppressed by undercooling. The nature of the crystallisation which takes place in an undercooled solid solution depends on the rate of formation of the different phases concerned, and on the extent of the undercooling with respect to each of these phases. A phase may even be produced which has no existence outside of the metastable region, and although this case may be exceptional, it is not legitimate to infer the structure of an undercooled alloy from a knowledge of the stable system alone.

Annealing either austenite or martensite at 650° causes resolution into ferrite and cementite, but the proportion of cementite produced is different in the two cases, and indicates that the needles of martensite contain only 0.3% of carbon. This suggests that martensite is a metastable solid solution of carbide in  $\beta$ -iron. Its transformation into the stable phases occurs at a much lower temperature than that of austenite. It is further shown that the change produced in austenite by cooling in liquid air consists in the crystallisation of a solid solution of low carbide content. This change takes place very rapidly. It is accompanied by expansion, and determinations with steel containing 1.79 and 1.50% of carbon respectively show that, whilst specimens quenched in different ways differ considerably in specific gravity, the differences become much less after quenching in liquid air. This gives a means of determining the proportion of austenite in a steel, and it is shown that

whilst autenite is only very slowly decomposed between  $0^{\circ}$  and  $270^{\circ}$ , it is rapidly decomposed above  $270^{\circ}$ . Martensite is very appreciably decomposed at  $90^{\circ}$ . All these observations are consistent with the supposition that martensite contains  $\beta$ -iron, and that its needle-like structure is due to its formation along the pre-existing cleavage planes of austenite.

C. H. D.

**Formation of Iron Rust.** GINO GALLO (*Gazzetta*, 1913, 43, i, 288—298).—From experiments on the solution tension of iron immersed in various electrolytes, especially sulphates, the author finds that rusting takes place the more rapidly the greater the difference of potential existing between the iron and the solution with which it is in contact. He suggests that the presence of sulphides may be a cause (in consequence of electrolytic phenomena) of the rapid rusting of iron. This conclusion is supported by other facts, including the analysis of very resistive irons of ancient origin; these contain very little sulphur.

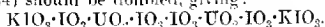
R. V. S.

**Formation of Rust under Protecting Paint [Coatings].** ERIC LIEBREICH and FRITZ SPITZER (*Zeitsch. Elektrochem.*, 1913, 19, 295—301. Compare A., 1912, ii, 259).—The authors have investigated the causes of rust formation on iron coated with pigments containing zinc oxide, lead carbonate, red lead, and ferric oxide. It is shown that in every case the rusting is due to an electrochemical action represented generally by the element: iron | moisture | colour substance. The electromotive force of a series of cells compounded of iron and the colour materials was measured. The colour substances were compressed into rods, which were then used as electrodes; the following cells were measured at  $20^{\circ}$ :  
 $\text{ZnO} | \text{KCl}, \text{H}_2\text{SO}_4 | \text{Fe} = +0.150 \text{ volt}; \quad \text{PbCO}_3 | \text{KCl}, \text{H}_2\text{SO}_4 | \text{Fe} = +0.095 \text{ volt};$   
 $\text{Pb}_3\text{O}_4 | \text{KCl}, \text{H}_2\text{SO}_4 | \text{Fe} = +0.075 \text{ volt};$   
 $\text{Fe}_2\text{O}_3 | \text{KCl}, \text{H}_2\text{SO}_4 | \text{Fe} = +0.090 \text{ volt}.$

The iron used in these measurements was pure, whilst if technical iron was substituted the values were from 0.02 to 0.04 volt higher. The probable causes of the *E.M.F.* generated in each case are discussed, and hypotheses put forward as to the reason for the rusting. The hypotheses are tested by means of *E.M.F.* measurements of a series of elements made up of the various substances under discussion.

J. F. S.

**Uranyl Iodates.** PAUL ARTMANN (*Zeitsch. anorg. Chem.*, 1913, 80, 280).—The formula given for the potassium uranyl iodates (this vol., ii, 224) should be doubled, giving:



C. H. D.

**Dehydration and Decomposition of the Hydrates of Uranyl Nitrate. Formation of a Monohydrate.** ROBERT DE FORCRAND (*Compt. rend.*, 1913, 156, 1044—1048).—Uranyl nitrate hexahydrate placed under a bell-jar with sulphuric acid in the cold at the ordinary pressure undergoes dehydration in two stages, as indicated by the rate of loss in weight. The first, lasting

for four to five days, corresponds with the formation of the trihydrate, and the second, complete at the end of one month, yields the dihydrate (compare Vasiliev, A., 1910, ii, 1072; Lebeau, A., 1911, ii, 403). Reduction of the pressure only increases the rate of the two stages. Dehydration of the dihydrate in a current of carbon dioxide, containing no nitrous vapours, at  $160^{\circ}$  yields the anhydrous salt in four hours, there being, at the same time, a considerable amount of decomposition with formation of uranic acid. If the temperature is lowered to  $125-130^{\circ}$ , the velocity of reaction is diminished to one-twelfth, and there is a short first stage corresponding with the formation of a monohydrate. Dehydration under similar conditions at  $98^{\circ}$  yields an almost pure monohydrate, containing less than 1% of uranic acid. By the admixture of nitrous fumes with the carbon dioxide, the products of dehydration were in accord with those obtained by Markéts (compare A., 1912, ii, 518). W. G.

**Synthesis of Borides in the Electric Vacuum Oven.** EDGAR WEDEKIND (*Ber.*, 1913, 46, 1198—1207).—Electrodes were made by submitting mixtures of the finely powdered constituents (boron and metal) to hydraulic pressure. These electrodes were then fritted, and afterwards used in the vacuum electrical furnace of the author to form an arc between; the heat thus produced brought about the formation of boride, which either melted and dropped off the electrode into a proper receptacle, or was deposited as a powder, because of the disintegration of the electrode, on an asbestos sheath arranged round the electrodes.

Zirconium boride,  $Zr_2B_3$ , has a shining, silvery appearance; D = 4.98—5.00, the hardness being 7 (compare Tucker and Moody, T., 1902, 81, 14). In the compact condition, it is only attacked by hydrofluoric acid, but when powdered, warm dilute hydrochloric acid dissolves it; nitric acid, dilute or strong, has very little action on the powder, and it is stable towards alkali hydroxides. It is attacked by fusion with sodium carbonate, and also by heating in a stream of chlorine.

[With C. Housr.]—*Vanadium boride*, VB, is metallic in appearance, and has a hardness greater than 7. It is stable towards alkalis and acids, with the exception of hydrofluoric and nitric acids, but is readily taken up by fused alkali hydroxide.

[With O. JACQUEM.]—*Tungsten boride*,  $W_2B_5$ , has properties similar to those of vanadium boride. Molybdenum boride could not be obtained in a pure condition, although a product corresponding approximately with the formula  $Mo_3B$  was obtained. Tucker and Moody (*loc. cit.*) have described a boride having the composition  $Mo_3B_4$ , but a repetition of their experiments gave a product containing 88% Mo and 9.9% B.  $Mo_3B_4$  requires Mo 86.7%, and since the product obtained is impure and nevertheless contains more than 86.7% Mo, it is improbable that it has the formula  $Mo_3B_4$ .

The results of Tucker and Moody with respect to tungsten boride,  $WB$ , were confirmed, but the density was 10.77 at  $20^{\circ}$ , as against 9.6 given by Tucker and Moody.

Titanium boride was not fully investigated; it appears to be fusible with great difficulty. T. S. P.

**Chinese Antimony Ores, Crude and Regulus.** WALTER R. SCHÖLLER (*J. Soc. Chem. Ind.*, 1913, 32, 261—262).—The crude antimony investigated by the author is obtained at Chang-sha, in the province of Hu-nan, by liquation, 50 lb. of the ore being heated at a time in clay crucibles, and fired for two hours. The amount of sulphur found in the crude antimony does not correspond with that required by the formula  $Sb_2S_3$ , there being always a deficiency, which is probably caused by the presence of oxide of antimony ( $Sb_2O_3$ ). Evidence for the presence of oxide is adduced by the fact that the liquated antimony sulphide is attacked by a solution of sodium hydrogen tartrate, whereby the antimony oxide is dissolved. Under like conditions stibnite is hardly attacked by the tartrate solution.

The antimony regulus obtained from the crude antimony apparently also contains oxide, but the amount of antimony dissolved by a solution of sodium hydrogen tartrate is much greater than the quantity of oxide assumed to be present.

In the sulphur assay of antimony sulphides the author finds that the most convenient method for eliminating the antimony is to precipitate it as antimonic acid by means of hot water. T. S. P.

**The System Antimony-Selenium.** NICOLA PARRAVANO (*Gazzetta*, 1913, 43, i, 210—220. Compare Chrétien, A., 1906, ii, 350; Pélabon, A., 1911, ii, 575, 899).—The author has investigated this system both by thermal analysis and by microscopic examination of the alloys. From the curves it appears that there is only one antimony selenide, which does not mix in all proportions with antimony. The two liquid layers in equilibrium contain respectively, 11% and 35% of selenium. The two non-miscible liquids discussed by Pélabon and Chrétien exist, but the difference in their densities is so small that there is no complete separation of them during cooling. The discontinuity in the curve between 60% and 70% of selenium is to be explained, not by the existence of a compound  $Sb_2Se_3$ , but as being due to partial miscibility of the compound  $Sb_2Se_3$  with selenium. Chrétien's selenides,  $SbSe$ ,  $Sb_2Se_3$ , and  $Sb_3Se_4$ , do not appear on the curve, and are not indicated by the microscopical examination. The two alleged alloys,  $SbSe$  and  $Sb_3Se_4$ , are mixtures of antimony with  $Sb_2Se_3$ . R. V. S.

**The System Bismuth-Selenium.** NICOLA PARRAVANO (*Gazzetta*, 1913, 43, i, 201—209).—The paper deals with the investigation of this system by the method of thermal analysis. The curve shows a discontinuity at about 73% of bismuth and 600—610°, and a maximum at about 63% of bismuth and 706°, which corresponds with the compound  $Bi_2Se_3$ . As the proportion of selenium is further increased, the curve falls, then remains horizontal, and finally descends to the m. p. of selenium. Various reasons are adduced, including arguments drawn from the microscopic appearance of the

alloys, to show that the thermal effect which mixtures containing 73–63% of bismuth show at 600–610° is due to the existence of the compound BiSe, which is of particular interest because in it bismuth is divalent.

R. V. S.

**Hydrolysis of Bismuth Nitrate.** ALFREDO QUARTAROLI (*Gazzetta*, 1913, 43, i, 97–124).—Measurements of the conductivity of solutions of bismuth nitrate containing excess of nitric acid show that strong hydrolysis occurs even in the presence of a considerable excess of nitric acid. The degree of hydrolysis under various conditions is shown by determinations of the concentration of the hydrogen ions, as indicated by the catalysis of methyl acetate. The dissociation constant of  $\text{Bi}(\text{NO}_3)_3$  calculated from these results is 0.0230. The formation of the sparingly soluble product  $\text{Bi}(\text{OH})_3 \cdot \text{NO}_3$  does not occur directly from  $\text{Bi}(\text{NO}_3)_3$ , but through an intermediate basic salt, probably  $\text{OH} \cdot \text{Bi}(\text{NO}_3)_2$ . The author shows by calculations from his experimental results how the phenomena observed on dilution of bismuth nitrate solutions may be explained, and the composition of the precipitates accounted for.

R. V. S.

**The Fluorides of the Noble Metals.** OTTO RUFF (*Ber.*, 1913, 46, 920–929).—If the fluorides of the noble metals could be obtained without having to use elementary fluorine, it would be possible to prepare fluorine by a chemical method by simply heating these fluorides.

[With WILLI JEROCH].—Attempts to prepare the fluorides of gold and platinum by decomposing the chlorides of these metals with anhydrous hydrogen fluoride or by fusion with potassium hydrogen fluoride were, however, unsuccessful.

The compound of platinum and hydrofluosilicic acid ("kieselflus-spatsäure Platinoxyd") described by Berzelius does not exist. Even solutions of platinum dioxide in concentrated hydrofluosilicic acid are strongly hydrolysed, and on evaporation give a residue of platinum dioxide hydrate, which contains only small quantities of platinum silicofluoride.

The addition of a solution of potassium fluoride to one of platinum tetrachloride gives an amorphous precipitate of *potassium perchlorohydroplatinite*,  $\text{K}_2(\text{PtCl}_5 \cdot \text{OH})$ , there being no fluorine in the precipitate.

[With F. EISNER].—The action of fluorine on various noble metals was studied by heating the metal, contained in a boat made of a mixture of cryolite and lithium fluoride, in a dry glass tube through which the gas was passed.

Ruthenium reacts with fluorine at 300°, but a sufficient quantity of the product formed could not be obtained for analysis. Iridium enters into reaction only at a dark red heat. Rhodium is scarcely attacked at a red heat. Palladium reacts slowly at a red heat. Osmium gives various fluorides (see next abstract).

T. S. P.

**Osmium Fluorides.** OTTO RUFF and FRIEDRICH WILHELM TSCHIRCH (*Ber.*, 1913, 46, 929–949).—Osmium forms three double,

namely, the *tetrafluoride*,  $\text{OsF}_4$ , the *hexafluoride*,  $\text{OsF}_6$ , and the *octafluoride*,  $\text{OsF}_8$ . They are obtained by the action of fluorine on heated osmium, the composition of the product (mixture) formed depending on the temperature, on the strength of the current of fluorine, and on the activity of the osmium preparation used, which activity depends to a great extent on the temperature to which the osmium oxide, from which the osmium was obtained, was heated. It was necessary to use a platinum tube for the fluorination, since the osmium fluorides are very sensitive towards glass.

At about  $250^\circ$ , using an active osmium preparation, the product obtained consists of the octa- and hexa-fluorides only, the proportion of the latter increasing as the strength of the current of fluorine diminishes. At lower temperatures, or by using a less active osmium preparation, the product formed is mainly the tetrafluoride.

Osmium octafluoride is separated from the other fluorides by simply evacuating the platinum tube at ordinary temperature and collecting in a dry glass receiver cooled by liquid air. It is a lemon-yellow, crystalline substance, melting at  $34.5^\circ$  to a yellowish-red liquid. The vapour is colourless, has a peculiar odour, and vigorously attacks the mucous membrane of the nose and eyes. The vapour pressures determined at various temperatures by the method of Smith and Menzies (A., 1910, ii, 687) are:  $38^\circ$ , 552.5 mm.;  $40.3^\circ$ , 594.5 mm.;  $42^\circ$ , 631.2 mm.;  $43.5^\circ$ , 655.6 mm.;  $47.3^\circ$ , 575 mm. From these figures the latent heat of vaporisation per gram is calculated to be 20.6 cal., between the temperatures  $38^\circ$  and  $54^\circ$ , the molecular latent heat being 7101 cal. The mean vapour density, determined by V. Meyer's method, was 355 (theory=343). When heated in a platinum tube, it begins to decompose at  $225^\circ$ , but the amount of decomposition is appreciable only above  $400^\circ$ . It attacks organic substances violently; the action on the various solid elements was also investigated. The aqueous solution is colourless, more or less hydrolysed, and has the odour of osmium tetroxide and not of the octafluoride. The solution in sodium hydroxide has the characteristic yellowish-red colour of the perosmic acids. With alkali fluorides it forms almost white salts (not investigated), which are decomposed by sodium hydroxide with evolution of ozonised oxygen.

The isolation of osmium octafluoride disposes of all doubts as to the octavalency of osmium.

Osmium hexafluoride is obtained, after removal of the octafluoride, by heating the platinum tube at  $50^\circ$  for one hour, the pressure being maintained at 20 mm. It sublimes, and condenses on the cool part of the tube as a light green, crystalline mass. It is difficult to obtain free from osmium dioxide and tetroxide, and a sufficient quantity of the pure compound could not be obtained to determine accurately its physical properties. The b. p. is about  $202\text{--}205^\circ$ ; the m. p. is above  $50^\circ$  and below  $120^\circ$ , but could not be determined accurately, as the compound becomes black on heating in contact with glass. It is decomposed by water and sulphuric acid, giving the osmium oxides and hydrofluoric acid. It dissolves



in sodium hydroxide, giving a yellowish-red solution, similar to that of sodium osmichloride.

The way in which osmium tetrafluoride is obtained has been indicated; the small quantities of the higher fluorides formed at the same time are removed by heating the platinum tube at  $100^{\circ}$  and passing a current of nitrogen through it at low pressure. If the residue is extracted with water, the tetrafluoride dissolves. It was not isolated, but if hydrofluoric acid is added to the solution in the proportion of 2 mols. of acid to 1 mol. of fluoride, and the solution then neutralised with potassium hydroxide and evaporated, regular crystals are obtained, which are probably potassium osmifluoride. The fact that osmium is present in the aqueous extract in the quadrivalent condition was proved by titrating the sulphuric acid solution with permanganate, whereby oxidation takes place to the octavalent condition; the oxidised solution liberates iodine from potassium iodide, the osmium being reduced to the quadrivalent condition. The quantities of permanganate used and iodine liberated were equivalent. A similar method of analysis was also used with the hexafluoride.

The following vapour pressures of osmium tetroxide were determined:  $95^{\circ}$ , 275 mm.;  $115^{\circ}$ , 182 mm.;  $125^{\circ}$ , 640.1 mm.;  $135^{\circ}$ , 779 mm. The m. p. is  $45^{\circ}$ . T. S. P.

### Mineralogical Chemistry.

**A Danger to be Guarded Against in Making Mineral Separations by means of Heavy Solutions.** WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1913, [iv], 35, 439--440).—It has long been known that certain minerals, especially metallic minerals, are acted on and decomposed by Sonstadt's (potassium-mercuric iodide) and Klein's (cadmium borotungstate) solutions. In the case now recorded there has been a replacement of calcium by an equivalent amount of potassium without the mineral being visibly affected. The material under examination was a canary-yellow, crystallised mineral, supposed to be carnotite, from Paradox Valley, Montrose Co., Colorado. It is a hydrous vanadate of calcium and uranium, differing from carnotite in containing calcium in place of potassium. This calcium carnotite is probably identical with the tyuyamunite of Xenadkevich (*Bull. Acad. Sci. St. Petersburg*, 1912, 945). By the action of Sonstadt's solution it is converted into ordinary carnotite with a decrease in the optic axial angle of  $25^{\circ}$ . Anal. I is of the untreated mineral, and II of another portion which had been treated for eighteen hours with Sonstadt's solution:

	$V_2O_5$	$UO_2$	$CaO$	$K_2O$	$CuO$ *	$SiO_2$	$P_2O_5$	$BaO$	$H_2O$
I.	18.03	53.71	5.29	0.21	4.16	2.45			61.13
II.	18.21	55.37	1.72	6.08	1.22	1.91			12.59

\* Copper, and possibly some of the calcium, present in an intermediate cadif vanadate.

L. J. S.

**Helium in Glucinum Minerals.** ARNALDO PIOTTI (*Atti R. Accad. Lincei*, 1913, [v], 22, 1, 140—144). The author has examined twenty-six minerals containing glucinum, but not radioactive, as to the amount of helium they contain. Taking into account the geological age of the various formations in which the specimens occurred, it is not possible to find any relationship between the amount of helium and the age of the mineral. Considerable variations also occur among the samples from the same locality. The beryls contain usually more helium than the chrysoberyls, whilst the phenacite ( $\text{Gl}_2\text{SiO}_4$ ) examined did not contain any. This observation excludes the possibility of the derivation of helium from glucinum.

R. V. S.

**Natural Thio-salts. I. The Plagionite Group.** FERRUCCIO ZAMBONINI (*Chem. Zentr.*, 1913, i, 739; from *Rec. Min. Crist. Italiana*, 1912, 41, 1—38).—A new source of plagionite is the Veta purissima pit in Oruro, Bolivia, where it is accompanied by crystalline and massive pyrites and lead-coloured clusters of needles or fibrous aggregates of meneghinite (jamesonite?), a transformation product of plagionite. The plagionite occurs in lead-coloured, lustrous lamellae, and rarely in single crystals, with  $a : b : c$  1.1305 : 1 : 0.8422,  $\beta = 107^\circ 15'$ . It has  $D^{25}_x$  5.54, and its analysis agrees with  $5\text{PbS}_4\text{Sb}_2\text{S}_3$ .

Spencer (*Min. Mag.*, 1909, 14, 303) expected that plagionite, heteromorphite, and samseyite would form a morphotropic group in which the PbS content increased by two molecules from step to step. A consideration of the best analyses and of the crystallographic constants, densities, and molecular volumes of the extreme members, however, leads the author to consider the plagionite group as a series of solid solutions of the end salts  $5\text{PbS}_4\text{Sb}_2\text{S}_3$ , plagionite, and  $5\text{PbS}_2\text{Sb}_2\text{S}_3$ , samseyite.

J. C. W.

**Bauxite or Sporogelite?** CORNELIUS DOELTER and EMIL DITTMER (*Centr. Min.*, 1913, 193—194. Compare A., 1912, ii, 357; 1913, ii, 230).—The name sporogelite has recently been proposed by Kipatie (this vol., ii, 61, 69) for the colloidal aluminium hydroxide which forms an important constituent of bauxite. The present authors prefer, however, to retain the old name bauxite for this constituent, and to refer to the mixture of minerals (that is, a rock) as bauxitite. It is urged that a definite formula ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) cannot be assigned to this mineral, but that, corresponding with the colloidal nature, the water may be variable in amount. L. J. S.

**Delafossite, a Cuprous Metaferrite from Bisbee, Arizona.** AUGUST F. ROGERS [with analysis by G. S. BOHART] (*Amer. J. Sci.*, 1913, [iv], 35, 290—294).—The mineral is found as indistinct platy crystals on hematite, and occurs together with native copper and cuprite in clay at the lowest zone of oxidation in the Calumet and Arizona mine. The crystals are rhombohedral ( $a : c$  1 : 1.91), with a black colour and streak and a metallic lustre:  $H = 5\frac{1}{2}$ . They are non-magnetic and easily fusible, and readily soluble in hydrochloric acid and sulphuric acid, but not in nitric acid. A soft, black,

graphite-like form with lamellar structure also occurs. Analysis gave:

Cu.	Fe.	Insol. (hematite).	O.	Total.
41.32	37.26	0.21	[21.21]	100.00

The ratios are very closely Cu : Fe : O = 1 : 1 : 2, and the formula may be written as  $\text{Cu}^{\text{I}}\text{Fe}^{\text{II}}\text{O}_2$ , cuprous metaferrite, or as  $\text{Cu}^{\text{II}}\text{Fe}^{\text{I}}\text{O}_2$ , cupric hypoferite. Qualitative tests show the presence of both ferrous and ferric iron; but it is pointed out that mixed solutions of cupric sulphate and ferrous sulphate react in the same manner. The first formula is regarded as the more probable. The well-known metaferrites (magnetite,  $\text{FeFe}_2\text{O}_4$ , etc.) of the spinel group are cubic in crystallisation; but the artificial sodium metaferrite,  $\text{NaFeO}_2$ , is rhombohedral and perhaps isomorphous with delafossite. The mineral delafossite was first described from Siberia by Friedel in 1873, and it has hitherto been looked on as a doubtful species.

L. J. S.

**Chromitite.** MILOKAD Z. JOVITSCHITSCH (*Bull. Soc. franç. Min.*, 1912 [i.e. 1913], 35, 511—516).—Analysis I. is of the black sand, in which the name chromitite was given (A., 1909, ii, 246), from the streams on the mountain Kopaonik, in Servia; and II—V of grains of the same mineral (II and III, dark brittle grains; IV and V, brighter and more resistant) isolated from a weathered mica-schists occurring in this district, and which is therefore to be regarded as the parent rock of the mineral chromitite:

	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	Total.
I.	30.59	6.23	59.68	1.25	3.89	101.64
II.	26.39	6.47	61.58	1.45	3.34	99.23
III.	27.13	8.77	61.35	1.21	3.19	101.55
IV.	22.53	8.45	63.37	1.35	2.98	98.68
V.	25.14	10.77	61.36	1.94	3.65	101.86

These analyses give the formula  $(\text{Fe},\text{Al})_2\text{O}_3 \cdot 2\text{Cr}_2\text{O}_3$ , differing from that previously given, namely,  $\text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ .

Chrome iron-ores which contain some ferric oxide may be regarded as mixtures of chromite,  $(\text{Fe},\text{Mg})(\text{Cr},\text{Fe},\text{Al})_2\text{O}_4$ , and chromitite,  $\text{Fe}_2\text{Cr}_2\text{O}_7$ .

L. J. S.

**Titaniferous Magnetite in the Basalt of Eresztövény, Hungary.** ALADÁR VENCLE (*Földt. Közl.*, 1912, 42, 911—914, 958—959).—A mineral occurring in the basalt of Eresztövény at the Medves Mountains, as black grains with a bright metallic lustre on its conchoidal fracture, has been referred to as ilmenite ("Titaneisen"). It is, however, strongly magnetic, and the following analysis proves it to be really a titaniferous magnetite:

$\text{TiO}_2$	$\text{SiO}_2$	$\text{FeO}$	$\text{Fe}_2\text{O}_3$	$\text{Mn}_2\text{O}_3$	Total.
6.58	trace	38.32	53.68	1.05	99.63

L. J. S.

**Two Varieties of Calciovolborthite (?) from Utah.** WILLIAM F. HILLEBRAND and HERBERT E. MERWIN (*Amer. J. Sci.*, 1913, 4v, 35, 441—445).—The minerals described occur as thin encrustations

together with other copper minerals, on sandstone near Richardson, in the canyon of Grand River, S.E. Utah. Both of them have the form of rosettes and patches of minute reticulated scales, and they are sometimes present together on the same hand-specimens. Only very limited amounts of impure material, consisting of scrapings from the sandstone surfaces, were available for examination. Analysis I (after deducting 30.6% of material insoluble in very dilute nitric acid) is of the yellowish-green variety. The optical characters of this indicate that the scales are probably monoclinic; and they show very strong inclined dispersion. Analysis II is of the greenish-yellow variety, which is probably pseudomorphous after the yellowish-green mineral. No definite formulae can be deduced from these analyses. I is a hydrous vanadate of copper, and II a hydrous arseno-vanadate of copper and calcium:

	V <sub>2</sub> O <sub>5</sub>	As <sub>2</sub> O <sub>5</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	CaO	BaO	MnO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	
I.	33.6	1.1	0.3	4.4	3.4	2.7	0.3	0.7	1.8	6.1	2.4	100
II.*	19.0	17.2	0.8	37.1	15.3	2.3	0.0	0.2	1.4	1.3	0.9	100.0

\* Also manganese, cobalt, and aluminium oxides, &c.

Very similar specimens have also been found in Paradox Valley, Montrose Co., Colorado.

L. J. S.

**Datolite from Mt. Mashuk, Caucasus.** NIKOLAI A. ORLOV (*Jahrb. Min.*, 1913, i, Ref. 38; from *Ann. Géol. Min. Russie*, 1911, 13, 146-148).—Previous analyses of the massive black mineral from this locality, near Pyatigorsk, did not lead to its correct identification, owing to the presence of impurities in considerable amount (A., 1912, ii, 950). Crystals of a black, grey (anal. I), and white (anal. II) colour have now been found, and the mineral is proved to be datolite. In the analyses, the boron was estimated by distilling the alkali fusion with methyl alcohol and hydrochloric or sulphuric acid, and collecting in a solution of potassium hydroxide:

	SiO <sub>2</sub>	TiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MnO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O	Total
I.	32.11	0.14	16.18	1.43	1.78	32.99	0.12	0.21	0.01	5.02	100.22
II.	37.25	—	21.26	0.21	0.19	36.41	0.15	n.d.	n.d.	5.21	100.74

PETR N. TSHIRVINSKI (*loc. cit.*, 166-171) also proves the identity of the massive mineral with datolite. It is rendered impure by intermixture with an amorphous, kaolin-like substance, hematite and other ores, elastic quartz and plagioclase, and calcite.

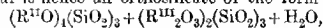
L. J. S.

**Chemical Examination of Certain Minerals from Ceylon Gravel.** GEORGI PROKOPVITSCH TSHERNIK (*Bull. Acad. Sci., St. Petersburg*, 1913, 163-174).—Gravel from the Sabaragamuwa Province of Ceylon contains small grey pebbles with a faint greenish tinge, the fresh fracture being almost pure black. The mineral gives a greenish-grey streak, and in thin sections permits a faint, bottle-green light to traverse it. It is not quite so hard as ortho-

class, and D has 3.76. Thin sections are seen to be non-homogeneous. Chemical analysis gives the results:

SiO <sub>2</sub>	CaO	Y <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	U <sub>2</sub> O <sub>7</sub>
30.91	16.82	0.17	10.48	8.18	12.82	0.07	10.06	2.07	4.61
ThO <sub>2</sub>	H <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O	Quartz	Total				
0.33	1.85	0.09	0.06	0.17	99.24				

The mineral is hence an orthosilicate of the form:



and is similar, but not identical with, orthite, which has the composition,  $6SiO_2, 3R^{III}_2O_3, 4R^{IV}O, H_2O$ .

T. H. P.

**Mineral Occurrences at Princeton, New Jersey.** ALFRED C. HAWKINS (*Amer. J. Sci.*, 1913, [iv], 35, 446—450).—Crystallographic descriptions are given of the various minerals (brookite, ilmenite, barite, chlorite, pyrite, calcite, and quartz), which are found as small, brilliant crystals in cavities and joints in brecciated sandstone in the neighbourhood of Princeton. Analysis, by A. H. Phillips, of the massive analcite, occurring together with crystals in the same district, gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	H <sub>2</sub> O	Total
53.79	23.58	14.35	8.36	100.07

L. J. S.

**Synthesis of Potassium-Nephelite.** GEORGES FRIEDEL (*Bull. Soc. franç. Min.*, 1912 [i.e. 1913], 35, 471—480).—Muscovite (anal. I) was heated with a solution of pure potassium hydroxide at 510—600° during forty to forty-five hours in a sealed steel tube with a copper lining. The copper was partly recrystallised, and the mica was transformed into a crystallised product identical with the mineral kaliophilite or potassium-nephelite. The crystals have the form of hexagonal prisms and plates, D 2.65; anal. II corresponds with the formula  $K_2O, Al_2O_3, 2SiO_2$ , with some of the alumina replaced by ferric oxide. Previous experiments made under similar conditions (Friedel, A., 1890, 1080) showed that when more than 2% of sodium hydroxide is present in the solution the crystallised product contains a predominating amount of the sodium molecule,  $Na_2O, Al_2O_3, 2SiO_2$ , as in natural nephelite. The potassium compound has been previously obtained by fusion with potassium fluoride, but in the form of orthorhombic crystals (Duboin, A. 1892, 1286).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total
I.	47.7	31.6	5.8	0.3	2.1	9.3	0.3	4.7	100.8
II.	57.2	26.2	6.6	—	—	28.6	0.9	—	100.5

It is therefore concluded that the potassium and sodium salts,  $R_2O, Al_2O_3, 2SiO_2$ , may be isomorphous, and that the explanation of the composition of natural nephelite given by Morozewicz (A. 1905, ii, 201) does not apply. To account for the excess of silica the recent theories of Foote and Bradley, Schaller, and Bowen are more likely to be correct.

L. J. S.

**Viridine, a Variety of Andalusite.** G. KLEMM (*Chem. Zentr.*, 1913, i, 54; from *Notiz. Ver. Erdk. Geol. Landesanst. Darmstadt*, 1911, 4—13).—A hornblende from the vicinity of Darmstadt contains a new mineral in the form of very small grains or columns of a green colour. It is rhombic, optically positive, and biaxial, has prismatic fracture, very strong pleochroism, double refraction (mean value 1.67), and considerable dispersion. Dittrich's analysis gave:

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Total.
85.30	1.04	55.52	4.15	4.77	169.79

which agrees with the formula (Al,Fe,Mn)<sub>2</sub>(Si,Ti)O<sub>3</sub>. The mineral is therefore an andalusite in which aluminium has been partly replaced by iron and manganese, and is similar in constitution and pleochroism to Bäckström's mangandalusite (A., 1897, ii, 271).

J. C. W.

**Minerals from the Ilmen Mtns., Urals.** W. SILBERMANTZ (*Jahrb. Min.*, 1913, i, Ref. 51—52; from *Trav. Soc. Natur. St. Pétersbourg*, 1911, 35, *Sect. Géol. et Min.*, 221—244).—Analysis I is of crystals of malacon; II, of brown aggrite; III, of green aggrite; and IV, of a felspar consisting of a perthitic intergrowth of albite and microcline, the former predominating. All these minerals were isolated from an aggrite pegmatite from the Roshkov spring:

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Ign.	Total.	Sp. gr.
I.	30.64	—	3.29	—	trace	—	—	—	—	0.95	100.55	4.51
II.	56.98	0.71	27.41	3.61	1.57	0.42	5.13	5.16	0.42	0.39	100.46	3.52
III.	54.14	1.12	28.21	1.76	1.08	0.19	2.89	5.93	1.19	0.83	100.81	3.39
IV.	65.18	18.60	1.60	—	—	0.17	0.34	8.97	5.15	0.47	99.31	2.587

\* Al<sub>2</sub>O<sub>3</sub> 65.67.

† Al<sub>2</sub>O<sub>3</sub> 9.33.

A mineral allied to parisite, from the Kyshtym district, and some other minerals are also described.

L. J. S.

**Alteration of Phyllite into a Compact Paragonite-rock.** FR. KILLIG (*Centr. Min.*, 1913, 263—269).—The following series of analyses, all of material taken from the same hand specimen, show the progressive replacement of potassium by sodium, the material having been transformed from a grey phyllite (anal. I) into white, shining scales of paragonite (anal. VI). The specimen came from the old emery mines on the Ochsenkopf, near Schwarzenberg, in Saxony. This alteration has taken place along crevices in the rocks of the district, and the paragonite is associated with corundum (emery) and metallic ores. The solutions which deposited the ores no doubt effected the change in composition of the rock. Several other analyses are given of the unaltered and partly altered phyllite:

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O	Total.
I.	43.09	0.57	38.03	0.83	1.90	0.82	1.11	1.12	7.31	5.33	109.11
II.	44.82	0.60	38.54	0.45	0.29	0.67	0.59	3.28	5.32	5.67	109.14
III.	44.54	0.62	38.79	0.11	0.15	0.19	0.36	4.87	3.88	5.58	99.99
IV.	43.86	0.57	37.21	0.13	1.90	0.78	0.28	5.23	3.62	5.80	99.95
V.	41.01	0.67	39.14	0.62	0.16	0.65	0.22	7.03	1.76	5.82	100.08
VI.	45.12	0.71	39.57	0.31	trace	0.49	0.11	7.94	0.17	5.50	109.22

L. J. S.

**Composition of Volcanic Magmas.** SANTIAGO PIÑA DE BOMES (*Anal. Fis. Quim.*, 1913, **11**, 238—248).—Two volcanic magmas from the Canaries consisted respectively of phonolite and basalt.  
G. D. L.

**Meteoric Iron from Perryville, Missouri.** GEORGE P. MERRILL (*Proc. U. S. Nat. Mus.*, 1912, **43**, 595—597).—This mass of iron, weighing about 17½ kilos, was found in 1906 near Perryville, in Perry Co., Missouri. The etched surface shows a very fine and somewhat irregular octahedral structure; and the metal is very hard and tough. Fragments showing no visible troilite have 0.76% The bulk analysis is given under I, and that of the schreibersite under II:

	Fe.	Ni.	Co.	Cu	Mn.	P.	S.	Si.	C.	Fe <sub>3</sub> O <sub>4</sub>	Total.
I.	99.015	0.680	0.545	0.025	nil	0.365	0.002	0.003	0.015	0.379	100.00
II.	51.10	34.13	0.30	—	—	14.00	—	—	—	—	99.53

Rare metals (iridium, palladium, platinum, ruthenium) are present as traces, although in variable quantities. In one portion of 25 grams was found 0.004 gram of platinum, and in another of 100 grams only 0.002 gram. The precipitates of ammonium platinum-chloride were in all cases coloured faintly orange, indicating the presence of palladium. In another 100-gram portion of the iron were found 0.014 gram of ruthenium and 0.028 gram of iridium, while yet another 100-gram portion yielded 0.0009 gram of ruthenium and 0.0011 gram of iridium. This appears to be the first record of the presence of ruthenium in meteoric iron.  
L. J. S.

## Analytical Chemistry.

**A New Form of Orsat Apparatus.** LOUIS M. DENNIS (*J. Ind. Eng. Chem.*, 1912, **4**, 898—901).—The improvement in the Orsat apparatus (*Chem. News*, 1874, **29**, 176) for the rapid estimation of carbon dioxide consists essentially of a new form of spiral pipette, whilst comparative sketches demonstrate other devices for rendering absorption complete.  
F. M. G. M.

**A New Dropping Apparatus for Use in Analyses.** O. RUDOLPH (*Chem. Zeit.*, 1913, **37**, 427).—A bulb-shaped glass container terminates below in a nozzle bent nearly at right angles. To the neck are fused two horizontal glass rods bent down at the ends, by means of which it may be suspended from the wall of a beaker in which a mechanical stirring operation is taking place. The reagent need not be introduced into the apparatus until this has been placed in its proper position.  
L. DE K.

**The Quantitative Handling of Small Quantities of Precipitates.** JULIUS DOXAU (*Monatsh.*, 1913, **34**, 553—560).—In the apparatus and methods previously described by the author (*A.*, 1911, ii, 225) there is a possibility that small quantities of the

precipitate may remain behind on the walls of the tube used, and thus escape weighing. Modifications of the apparatus are now described, which do away with this error. Small platinum dishes are used to carry out the precipitation in, and these are tared, together with the filters used, both before and after the experiment, so that no part of the precipitate remains unweighed. Details are given of the results obtained in the gravimetric estimation of mercury, arsenic, iron, copper, chlorine, calcium, and sulphates.

It is claimed that there is a considerable saving of time when such micro-methods are used. For example, the estimation of chlorine in a soluble chloride is easily completed in half an hour.

T. S. P.

**Application of New Results of the Investigation of Indicators to Quantitative Studies.** ALFRED TRIEL (*Chem. Zentr.*, 1913, i, 653; from *Sitzungsber. Ges. Beförd. ges. Naturwiss. Marburg*, 1912, 6, 54 pp.).—An attempt has been made to combine Hantzsch's conception of the colour change of indicators as being due to chemical rearrangements with Ostwald's theory of indicators, which employs the ionic theory and the law of mass action. By means of calculations from measurements on the sensitiveness of methyl-orange and phenolphthalein culled from the literature, a further attempt has been made to provide a clear idea of the adaptability of these indicators to common titrations. A strong acid (hydrochloric) and a strong base (sodium hydroxide) were chosen as standard solutions, and strong, weak, and very weak acids and bases (hydrochloric acid, acetic acid, and phenol; sodium hydroxide, ammonia, and *p*-chloroaniline) were titrated, the dilution being such that all the involved substances could be considered as completely dissociated. "Titration curves" are given connecting the initial hydrogen-ion concentration with the volume of standard solution added, and the influence of dilution and temperature on these curves is shown.

J. C. W.

**Ferrous Sulphate Monohydrate and its Use in Volumetric Analysis.** DANIEL FLORENTIN (*Bull. Soc. chim.*, 1913, [iv], 13, 362—366).—It is pointed out that the monohydrated form of ferrous sulphate is readily obtained pure, is not hygroscopic, and can be kept for long periods without change, so that it is suitable for use in standardising oxidising solutions such as potassium permanganate solution.

The salt is prepared by dissolving 400 grams of ferrous sulphate, previously crystallised several times, in 200 c.c. of 50% sulphuric acid by warming gently on a water-bath. Almost as soon as solution is complete, the monohydrate begins to separate as a colourless, crystalline powder, which is collected on a Büchner filter, washed with alcohol or dry acetone, then with dry ether, and is finally dried under reduced pressure over sulphuric acid. The yield is about 40 grams.

T. A. H.

**New Colour Reactions of Hydrogen.** ANGEL DEL CAMPO Y CERRDAS (*Anal. Quim.*, 1913, 11, 172—178).—Polemical against



Giral (this vol., ii, 147). The author points out that numerous colour reactions of reduction, for example, with molybdic, arsenic, molybdic, vanadic, phosphovanadic, tungstic, phosphotungstic, and silicotungstic acids, may be obtained by the aid of Zeugelig's platinum method (A., 1910, ii, 1106).

G. D. L.

**Direct Estimation of Water in Food-stuffs and Other Articles by Distillation.** FRANZ MICHEL (*Chem. Zeit.*, 1913, 37, 353—355).—The principle of the method is as follows: The substance in which the water is to be estimated is distilled with an excess of an indifferent liquid, which is insoluble in and lighter than water, and has a higher boiling point than water. The indifferent liquid used is a mixture of pure toluene and commercially pure xylene in the proportion of 1:2 by volume. The vapours from the distilling flask are condensed in a condenser which opens on to a funnel connected with a graduated tube. When the distillation is complete, the contents of the tube are left until the water has settled to the bottom, when its volume may be read off, making appropriate corrections for the effect of the toluene-xylene mixture on the meniscus. It is an advantage to centrifugalise the contents of the tube in order to bring about rapid separation.

The method was tested on honey, butter, and milk, and found to give good results.

T. S. P.

**The Estimation of Chlorine in Urine and Blood.** K. O. LARSSON (*Biochem. Zeitsch.*, 1913, 49, 479—485). Chlorine can be directly estimated in urine by direct titration with silver nitrate and the use of potassium chromate as an indicator, if the urine (diluted if necessary so that the sp. gr. is not higher than 1025) is first treated with pure animal charcoal (1 gram to 20 c.c. urine). By this means the purine substances which interfere with the titration are removed. A similar method is applicable to the estimation of chlorine in blood; 5—10 c.c. of blood are treated with 50 c.c. of hot 2% magnesium sulphate solution and a little acetic acid, and the mixture is heated on a water-bath until the coagulation of proteins is complete. After cooling, the liquid is diluted to 100 c.c. and then treated with about 3 grams of charcoal. The chlorine titration is then carried out with 50 c.c. of the filtrate.

S. B. S.

**Estimation of Chloride and Bromide in Organic Fluids.** STEFAN VON BOGÁNDY (*Zeitsch. physiol. Chem.*, 1913, 84, 14—14). An apparatus for the estimation of the halogens in blood and similar organic fluids is described and figured. The fluid is heated in a Jena flask in a stream of air with concentrated sulphuric acid, copper sulphate, and potassium sulphate. The escaping vapours pass through a spiral wash bottle containing silver nitrate and are provided with a glass stopper at the bottom, which can be removed. A second such wash-bottle is attached for safety. The precipitate of mixed silver haloids is collected in a filter tube, and after weighing a stream of chlorine is passed through to convert the whole into silver chloride.

E. F. A.

**Guareschi's New Bromine Reaction for the Detection of Bromate in Potassium Chlorate.** FRANCESCO NUOLA (*Chem. Zentr.*, 1913, i, 461; from *Giorn. Farm. Chim.*, 1912, 61, 538—541. Compare Guareschi, A., 1912, ii, 989; this vol., ii, 333).—The author describes the successful application of Guareschi's reaction to the detection of small traces of potassium bromate in potassium bromide. When testing for bromates in potassium chlorate, it is best to ignite the sample and to apply the test to the chloride.

J. C. W.

**Detection of Iodine in Concentrated Solutions Rich in Magnesium Salts.** HEINRICH FRESenius (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 118—120).—See this vol., ii, 401.

**Detection and Estimation of Fluorine in Wines.** F. COMA Y ROCA (*Anal. Fis. Quim.*, 1912, 10, 469—477).—The uncorrected error in Fresenius's method for the determination of fluorine amounts, according to the author, to +2.1, and after correction to -4.4%. More accurate results were obtained by using all-glass apparatus and boiled sulphuric acid. In application to the estimation in wines the errors, both by gravimetric and volumetric methods, are considerable (in the latter about 8%). Qualitatively, 1 mg. of sodium fluoride in 300 c.c. of wine may be detected.

G. D. L.

**Estimation of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace.** W. H. WALKER and WALTER A. PATRICK (*J. Ind. Eng. Chem.*, 1912, 4, 792—801. Compare A., 1912, ii, 995).—A sketch of the apparatus employed with a preliminary account of the procedure whereby the oxygen in iron and steel can be estimated by conversion of the metallic oxides into carbides by heating with an excess of carbon in an electric furnace, with the quantitative formation of carbon monoxide.

The metal (20–25 grams) is mixed with powdered graphite in a graphite crucible, placed in an electric vacuum furnace of the Arsen type, the pressure reduced to 0.01 mm., and the crucible heated at 500–600° during fifteen minutes, allowed to cool, and any adhering oxygen washed out with perfectly dry nitrogen, this process being repeated until the absence of oxygen is ensured.

A current of about 300 amperes is passed; the metal fuses, when violent ebullition often occurs, which must be moderated by opening the circuit; after about twenty minutes' heating, the furnace is cooled, dry nitrogen admitted, and the gas removed in convenient volumes into an apparatus, where the carbon monoxide is estimated by passing it over iodine pentoxide at 130° (Kinnicutt and Sanford, A., 1900, ii, 314). By heating at 130° (instead of 150°) oxidation to carbon dioxide is complete, and the decomposition of the iodine pentoxide is reduced to a minimum, which was a difficulty previously experienced in this method (*loc. cit.*).

F. M. G. M.

**Sulphur and its Variations in the Biological Treatment of Sewage Water.** LUCIEN CAVEL (*Compt. rend.*, 1913, 156, 1099—1101).—A determination of the amount of sulphur combined in the form of organic matter in the sewage effluent gives a measure of its purification. The examination is conducted as follows: The effluent is allowed to remain for three hours, when the heavier particles settle, and then to it is added zinc chloride, followed by sodium carbonate in suitable quantity. The precipitate, which carries down with it all suspended matter, is collected, dried, and extracted with carbon disulphide, thus giving the free sulphur. The residue is washed with benzene and decomposed by hydrochloric acid, the hydrogen sulphide liberated being weighed as silver sulphide, which gives the sulphur in the form of sulphide. To the residue, sodium hydroxide is added, and the whole is heated at 80° for six hours, after which chlorine is passed through the liquid. The combined sulphur, now converted into sulphate, is weighed as barium sulphate, thus giving a measure of the purity of the effluent. W. G.

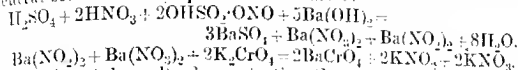
**Assay of Hyposulphites** EMIL BOSSHARD and W. GROB (*Chem. Zeit.*, 1913, 37, 423—426, 437—439).—*By Means of Ammoniacal Copper Sulphate.*—About 0.1 gram of the sample is placed in a corner of the bottom of a flask, and while slightly inclining the flask an ammoniacal solution of copper sulphate (4.469 grams of crystallised copper sulphate per litre) is added from a burette in quantity sufficient to complete the reaction within a few c.c. The liquid is now allowed to come in contact with the solid, and after shaking 2 drops of indigo carmin (1 gram per litre) are added. The titration is continued until the yellow colour changes to a clear blue. Two mols. of copper : 1 mol. of sodium hyposulphite. All the operations are carried out in the author's special apparatus in a current of oxygen-free nitrogen or hydrogen. The usual impurities present in commercial samples do not appreciably affect the result.

*By Acidimetry.* The sample is oxidised by atmospheric oxygen, and the acidity is then estimated as usual, preferably with standard barium hydroxide; allowance should be made for any pre-existing acidity, which must be determined in a current of hydrogen.

*By Means of Mercuric Chloride.*—To 300 c.c. of a saturated solution of mercuric chloride is added 1 gram of sodium hydrogen carbonate. A weighed quantity of the sample is then added, and the precipitate consisting of mercury and mercurous chloride is collected on an asbestos Gooch crucible, and washed first with dilute hydrochloric acid and then with water. The whole is then placed in a beaker and treated with 5 grams of potassium iodide and 5 c.c. of water, followed by 5 c.c. of *N* 10 iodine. After ten minutes with frequent stirring, the excess of iodine is titrated with thiosulphate.

If the number of c.c. of iodine absorbed is represented by *a*, and the weight of the sample taken by *x*, the percentage will be according to the formula  $\% = 171.14 \times 2000 \div 0.87071 a$ . L. DE K.

**The Quantitative Estimation of Sulphuric, Nitric, and Nitrous Acids in Mixed and Waste Acids.** GEORGE FISCH (*Zeitsch. ges. Schiess-Sprengstoffw. u. Min.*, 1912, 7, 337—339. Compare Telle, A., 1906, ii, 578).—A modification of the method previously described (A., 1912, ii, 991), in which, after titrating the total acidity with barium hydroxide and separating the barium sulphate, the neutral mixture of barium nitrate nitrite is titrated with a neutral solution of *N*/5 potassium chromate:



Experimental results demonstrating the accuracy of the method are tabulated in the original.

F. M. G. M.

**Apparatus for Fumeless Kjeldahl Nitrogen Digestion.** ALBERT P. SY (*J. Ind. Eng. Chem.*, 1912, 4, 640).—A group of four of the ordinary long-necked Kjeldahl flasks supported in a line on iron rings are closed by loosely fitting bulb-tubes consisting of a tube with two large bulbs with an elbow bend; each of these are connected by rubber tubing with a suction pump, having four branches. These bulbs act as air condensers for the acid fumes, and prevent the liquid in the flasks from evaporating as rapidly as if the fumes are allowed to escape.

F. M. G. M.

**Estimation of Nitrites in Potable Water.** MAURICE LOMBARD (*Bull. Soc. chim.*, 1913, [iv], 13, 304—309).—The estimation of nitrites in potable water by means of *m*-phenylenediamine or of sulphanilic acid and  $\alpha$ -naphthylamine is rendered tedious by the somewhat fugitive nature of the colorations obtained and the necessity of preparing a new scale of tints for each series of tests. The author proposes the use of the following reagent, the tints obtained with which very closely resemble those given by suitably diluted solutions of potassium dichromate which form the scale of comparison: sulphanilic acid (1 gram) is dissolved in a saturated solution of ammonium chloride (100 c.c.); phenol (1·5 gram) is then added, followed by approximately 2*N*-hydrochloric acid (100 c.c.). In practice, the reagent (1 c.c.) is added to the water (50 c.c.), which, after the lapse of at least fifteen minutes, is rendered alkaline by addition of an excess of ammonia. The coloration obtained is then compared with those of previously standardised solutions of potassium dichromate. By this method, 0·1 mg. of sodium nitrite per litre could be estimated, which is regarded by the author as the limit of useful accuracy. If, however, traces of nitrites are to be detected, he prefers to use sulphanilic acid and  $\alpha$ -naphthylamine. If the reagent is to be preserved during considerable periods, replacement of the acid by water is recommended. Immediately prior to use, it is then acidified with an equal volume of hydrochloric acid.

H. W.

**Estimation of Phosphorus in Iron and Steel.** PAUL ARTMANN [and J. PREISINGER] (*Zeitsch. angew. Chem.*, 1913, 26, 203—208).—A review and criticism by the first author of the various methods used for the above estimation. A new method has been worked out by the authors, which is, briefly, as follows.

The sample (about 1 gram for pig-iron, 2—4 grams for steels) is dissolved in nitric acid; any graphite is removed by filtration. The phosphorus is fully oxidised by means of permanganate, and then precipitated with molybdate solution.

The filter and precipitate after being carefully washed are replaced in the flask, 10 c.c. of standardised hypobromite solution are added, and then 7 grams of sodium hydrogen phosphate. After diluting to 80 c.c., 0.5 gram of potassium iodide is added, and then 15 c.c. of 4*N*-sulphuric acid. The iodine liberated is then titrated with  $N/20$ -thiosulphate solution.

The difference between the blank check and the result obtained represents the ammonia in the yellow precipitate, and hence the phosphorus.

The hypobromite is conveniently prepared by pouring 1400 c.c. of saturated bromine water into 500 c.c. of 4*N*-sodium hydroxide.

L. DE K.

**Estimation of Phosphorus in Commercial Acetylene.** LOUIS M. DENNIS and W. J. O'BRIEN (*J. Ind. Eng. Chem.*, 1912, 4, 834—836).—A modification of the method described by Lunge and Cedercreutz (A., 1898, ii, 54) for estimating the gaseous compounds of phosphorus present in acetylene which has been prepared from calcium carbide. The acetylene is generated in a Kipps apparatus with a saturated solution of sodium chloride, and obtained without any appreciable rise of temperature; a Friedrich's gas-washing bottle is considered a more efficient absorption apparatus than the ten bulb-tubes employed by Lunge (*loc. cit.*), and the hydrogen phosphide after absorption by sodium hypochlorite is estimated as magnesium pyrophosphate.

F. M. G. M.

**The Assay of Hypophosphorous Acid.** HORACE NORTH (*Amer. J. Pharm.*, 1913, 85, 147—148).—Samples containing excessive amounts of foreign acids (sulphuric, oxalic, tartaric, phosphoric, phosphorous) are readily recognised by their excessive barium number, which the author states should not exceed 5.

The details are as follows: Weigh 1 c.c. of the sample in a carefully tared, stoppered Erlenmeyer flask. Add 20 c.c. of water free from carbon dioxide, and titrate with  $N/5$ -barium hydroxide with phenolphthalein as indicator. When the precipitate has subsided it is collected, well washed, dried, and ignited. The corrected weight in milligrams divided by the weight in grams of absolute acid as indicated by the titration is called by the author the "barium number."

L. DE K.

[**Estimation of] Arsenic in Zinc.** SIDNEY CROOK (*Chem. News*, 1913, 107, 149).—The granulated sample is sieved through a

24-hole sieve. The Marsh's apparatus should be fitted with a half-inch glass tube containing a roll of lead acetate paper, and about 6 inches of fused calcium chloride, and also with a mirror tube. The hole of the inlet tap of the apparatus should be about one-eighth of an inch in diameter, so as to admit the granulated sample. The apparatus is charged in the usual way with arsenic-free zinc (20 grams) and sulphuric acid (30 c.c. of recently boiled and cooled dilute acid), and when free from air and the action almost ceased, 20 c.c. of recently boiled distilled water and 0.5 gram of the sample are put in the thistle funnel. The hydrogen flame is then put out, a small Bunsen burner placed beneath the mirror tube, and when the tube is nearly red-hot its outlet is stopped up with the thumb in order to cause a gentle back pressure. On opening the tap of the thistle funnel, the whole of the sample of zinc can be caused to fall into the apparatus, without air entering. The tap is then closed, the water withdrawn from the funnel and replaced by 30 c.c. of dilute sulphuric acid, sufficient of which is then run into the flask to keep the hydrogen flame not more than  $\frac{1}{4}$  inch in height. The reaction should be continued for half-an-hour, after which the mirror of arsenic obtained is compared with a set of standard mirrors. The sample should be so arranged as to give not more than 0.1 mg. of arsenic.

T. S. P.

**Rapid Estimation of Boric Acid in Milk and Cream.** FREDERIC W. RICHARDSON and WILLIAM KEIGHTLY WALTON (*Analyst*, 1913, 38, 140-141). To 50 c.c. of milk or 10 grams of cream diluted with 40 c.c. of water are added 5 c.c. of 5% copper sulphate solution, and after heating to boiling the casein-copper precipitate, which carries down the fat, is collected and washed several times with boiling water. The filtrate is then used for the estimation of the boric acid as follows:

Two c.c. of a 1% alcoholic solution of phenolphthalein are added, and then  $N/10$ -sodium hydroxide until a certain blue shade appears. About one-third of the volume of glycerol is now added, and the titration is repeated until the blue shade again appears. Under these conditions 1 c.c. of  $N/10$ -alkali = 0.0071 gram of crystallised boric acid.

L. DE K.

**Combined Estimation of Boric Acid and Fat in Cream.** FREDERIC W. RICHARDSON (*Analyst*, 1913, 38, 141-142).—"The fat in cream (see preceding abstract) may be readily recovered from the 'casein precipitate' by drying the filter and contents in the mouth of a short-necked counterpoised flask in a water-oven. The filter is then lifted out, and placed in a Soxhlet tube, which is attached to the flask, into which most of the fat has already collected. Light petroleum (of low b. p.) is then used for the extraction as usual.

L. DE K.

**Estimation of Total Carbon in Steel and Ferro-Alloys by Combustion in Oxygen under Pressure.** W. G. VON JOHN (*Chem. Zeit.*, 1913, 37, 426-427).—"The sample is placed in a

crucible made of asbestos, or preferably of magnesia, and burnt at 1 atmospheric pressure in an atmosphere of purified oxygen in the special apparatus devised by the author. The combustion is started by electrical contrivance.

The products of combustion find their way into a solution of sodium hydroxide (4 grams per litre), the excess of which is then titrated with standard sulphuric acid (4.083 grams per litre), using phenolphthalein as indicator; 1 c.c. of acid=1 mg. of carbon. When dealing with alloys, the combustion should be assisted by means of lead peroxide.

L. DE K.

**The Estimation of Carbon by Combustion in Moist Oxygen.** SIEGFRIED HILPERT (*Ber.*, 1913, 46, 949-952).—In the estimation of carbon in steels, by combustion in dry oxygen, it is necessary to heat to a temperature of about 1200°. If moist oxygen is used, a temperature of 950° is sufficient in the case of ordinary, chrome, and chrome-tungsten steels; for 80% ferromanganese, containing 6.16% C. a temperature of 1050° is necessary.

In the case of certain organic compounds, such as aluminium phenyl, hippuric acid, glycine, alanine, carbazole, phenyl dihydrogen phosphate, etc., which are difficult to burn satisfactorily, accurate results are obtained with moist oxygen at lower temperatures than ordinarily used.

When using moist oxygen, a 5 cm. long, straight, phosphoric oxide tube should be inserted between the calcium chloride tube and the potassium hydroxide bulbs. If the hydrogen also is to be estimated, the combustion should be carried out in the ordinary way until carbonisation is complete, after which the calcium chloride tube is changed and the combustion finished with moist oxygen.

T. S. P.

**Estimation of Carbon Dioxide in Carbonates.** FRANK S. SINNATT (*Analyst*, 1913, 38, 136-140).—A complicated apparatus, being in part that described previously (*A.*, 1912, ii, 679), is used. The carbonate is decomposed by means of dilute hydrochloric acid, and the gases evolved are passed over calcium chloride and silver sulphate, and find their way into an exhausted flask; before starting, the whole of the apparatus has been swept by a current of purified air.

The last traces of carbon dioxide in the liquid are expelled by heating. Finally, a known volume of standard barium hydroxide is admitted into the flask, purified air is transmitted until normal pressure is restored, and the excess of barium hydroxide is then titrated as usual.

L. DE K.

**A New Apparatus for the Estimation of Carbon Dioxide.** E. W. GAITHER (*J. Ind. Eng. Chem.*, 1912, 4, 611-612).—A description, with sketch, of an apparatus for the estimation of carbon dioxide in soils by the double titration method; the advantages claimed are: that it does not require to be taken apart for any of the operations involved; it contains no delicate, easily broken

parts; it can be employed at atmospheric pressure or under a diminished pressure of 70 cm., and that one person can simultaneously keep six experiments working, and complete thirty-six estimations in an eight hours' day.

F. M. G. M.

**A New Apparatus for the Volumetric Estimation of Carbon Dioxide.** HOWARD W. BRIDGEMAN (*J. Ind. Eng. Chem.*, 1912, 4, 599).—A criticism of the apparatus previously described for this purpose by Bowser (*A.*, 1912, ii, 995), with a sketch of one the author considers more easily manipulated. The carbon dioxide is passed into a closed graduated conical flask containing potassium hydroxide, the air aperture in which consists of a glass tube with a widened base, filled with glass beads and resting on the bottom of the flask. The subsequent titration is carried out without transferring the distillate.

F. M. G. M.

**A Carbon Dioxide Absorption Bottle.** W. A. KOENIG (*J. Ind. Eng. Chem.*, 1912, 4, 844).—The bottle, which is 12 cm. high and 3.5 cm. wide, is fitted at the neck with an inlet-tube and at the base with an outlet-tube, each of which are furnished with a mercury "trap." The interior of the bottle is packed with soda-lime at the top and calcium chloride at the bottom, and the weight when thus prepared does not exceed 50-60 grams; it can be employed for about one hundred estimations of carbon dioxide in steel drillings without re-charging.

F. M. G. M.

**Estimation of Colloids in Arable Soils.** MARYAN GÖRSKI (*Zeitsch. landw. Vers. Wesen. Oesterr.*, 1912, 15, 1201-1216).—From the result of numerous experiments on the absorption of colloids in soils by crystal-violet, the formula suggested by Freundlich (*A.*, 1907, ii, 155, 534, 939) is considered correctly to represent this reaction; the author is also in agreement with the results of König, Hasenbäumer, and Hassler (*A.*, 1911, ii, 1033).

F. M. G. M.

**New Methods of Soil Analysis and the Estimation of Colloids in Soils.** RUDOLF VAN DER LEEDEN and F. SCHNEIDER (*Bied. Zentr.*, 1913, 42, 145-147; from *Intern. Mitt. Bodenkunde*, 1912, 2, 81).—Experiments with soils produced by the weathering of gneiss indicated that for the comparison of the hygroscopicity of a soil with that of the silicates dissolved by hydrochloric acid, extraction with aqueous hydrochloric acid is unsuitable, since the solution of colloidal silica, its precipitation with adhering oxides of iron and aluminium and other dissolved substances, introduce errors. The acid may also dissolve colloids which possess only slight hygroscopicity: this could be avoided by employing gaseous hydrogen chloride.

The assumption that the absorption of dyes rises and falls with the amount of colloids is not accepted. Exact experiments on the absorption of dyes and hygroscopicity can only be made when the surfaces of the soils are estimated on the one hand by the employ-



ment of a dye solution, and on the other by using the vapours of organic substances of high molecular weight.

The results of analyses as well as estimations of hygroscopicity indicated that unweathered minerals are dissolved by hot hydrochloric acid.

N. II. J. M.

**Estimation of Potassium as Platinichloride.** GEDEON MEILLÈRE (*J. Pharm. Chim.*, 1913, [vii], 7, 281—282).—In order to obtain a potassium platinichloride free from the sodium compound, the use of acetone is recommended instead of alcohol generally employed.

If an insufficiency of platinum chloride has been used, the residue may contain a little sodium chloride; this, however, is of no consequence if the platinum is finally weighed as metal.

L. DE K.

**Detection of Potassium with Tartaric Acid.** LUDWIG W. WINKLER (*Z.-tsch. angew. Chem.*, 1913, 26, 208).—The author has observed that tartaric acid in powder is a more delicate reagent for potassium than a solution of the acid. The reaction may be applied as follows: To 10 c.c. of the neutral solution is added 0.5 gram of crystallised sodium acetate, and then 0.5 gram of tartaric acid in fine powder; a precipitate forming rapidly on shaking proves the presence of potassium. Ammonium, rubidium, and caesium should, of course, be absent.

L. DE K.

**Estimation of Lithium.** LESLIE RUSSELL MILFORD (*J. Ind. Eng. Chem.*, 1912, 4, 595—597).—The mineral water (200–500 c.c.) is evaporated to dryness with hydrochloric acid, and the silica dehydrated at 120°; the residue, after moistening with hydrochloric acid, is treated with about 25 c.c. of 95% alcohol, and the precipitate collected and washed with the same until free from lithium; the alcoholic solution is evaporated to dryness, and the process repeated with hydrochloric acid and absolute alcohol. The residue, after treating with dilute hydrochloric acid, is rendered alkaline with calcium hydroxide, whereby the magnesium is precipitated as magnesium hydroxide; the calcium is then separated as oxalate, and after twelve hours the filtrate, which practically contains only lithium and ammonium salts, is evaporated and the latter expelled by heating in the usual manner.

The acidified (hydrochloric acid) aqueous solution of the residue is treated with about 30 c.c. of amyl alcohol, the water boiled away, and the filtered solution evaporated to dryness with dilute sulphuric acid; the lithium solution is evaporated down and weighed as lithium sulphate, from which 0.0017 gram must be deducted to correct for the solubility of sodium and potassium chlorides in amyl alcohol. The advantages claimed are: Waters containing many chlorides can be handled with ease without loss of lithium by decrepitation; large volumes of water can be employed; the employment of calcium instead of barium hydroxide does not introduce another metal, and the calcium oxalate precipitate is more insoluble than barium oxalate.

F. M. G. M.

**Estimation of Calcium as Tungstate.** A. SAINT-SERNIN (*Compt. rend.*, 1913, 156, 1019—1020).—By addition of excess of a 20% solution of normal sodium tungstate to a boiling ammoniacal solution of calcium chloride, the calcium is completely precipitated in a heavy, crystalline form as calcium tungstate,  $\text{CaWO}_4$ . This is filtered, washed and dried at 100°, and weighed as such. Magnesium not being precipitated under these conditions, it furnishes a ready method for the separation of these two elements in analysis.

W. G.

**Assay of Barium Sulphate in Radiographic Examinations.** GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1913, [vii], 7, 282—283).—For the above purposes, barium sulphate, in itself perfectly inert, should be quite free from soluble (toxic) barium salts. Fifteen to twenty grams of the commercially pure article are treated with 100 c.c. of 10% hydrochloric acid. After adding a little filter paper pulp and filtering, the clear filtrate is tested for barium by means of sulphuric acid and also with ammonia and potassium dichromate. L. DE K.

**Estimation of Zinc by Electroanalysis.** ELLWOOD B. SPEAR and SAMUEL S. STRAHAN (*J. Ind. Eng. Chem.*, 1912, 4, 889—890, Compare A., 1910, ii, 455).—The electrolytic method of estimating zinc described by Kemmerer (A., 1911, ii, 335) is considered the most satisfactory when the following modifications are introduced: (a) Cooling the solution for a few minutes before the end of the experiment; (b) reducing the amount of potassium hydroxide employed; and (c) the employment of a rotating nickel gauze cathode and a stationary platinum plate or spiral anode. The method is shown to entail a compensation of errors, the chief of which are: (1) loss of zinc in the wash-bottle, counterbalanced by the formation of zinc hydroxide on the cathode; (2) the effect of air on an exposed cathode; (3) oxidation of the deposit by anode gases; (4) effect of temperature at the beginning and end of the electrolysis; (5) the effect of ether containing water and oxides on the deposit; (6) a high result from allowing the ether to evaporate off the cathode in a desiccator; (7) the presence of nitrates.

F. M. G. M.

**Estimation of Lead in Lead Paints.** JULIUS F. SACHNER (*Chem. Zentr.*, 1912, ii, 2147; from *Farbenzeit.*, 1912, 18, 295—296).—All new methods for the estimation of lead in paints, including Utz's electrolytic process (this vol., ii, 76) give untrustworthy results. A correct method is that of Schindler and Alexander (Lunge, *Tech. Methods of Chem. Analysis*; compare A., 1893, ii, 599), which is based on a titration with ammonium molybdate. J. C. W.

**Separation of Small Quantities of Mercury by Electrolysis.** OTTO SIEGUM (*Zeitsch. physiol. Chem.*, 1913, 84, 239—242, Compare Buchta, this vol., i, 318; Salkowski, this vol., i, 562).—Polemical. The author's electrolytic method for separating mercury (A., 1905, ii, 486) is upheld in all its details. E. F. A.

**Reactions of Mercuric Compounds.** MORITZ KOHN and ALFONS OSTERSETZER (*Zeitsch. anorg. Chem.*, 1912, 80, 218-229).—The estimation of mercuric haloids by means of hydrogen peroxide and alkali (A., 1908, ii, 892) may be improved by using sodium peroxide free from halogen. The salt is boiled with water and a slight excess of sodium peroxide, the precipitated mercury is repeatedly washed, and the halogen is estimated in the filtrate. Mercuric iodide requires a large excess of peroxide, otherwise reduction is incomplete.

The arsenite method (A., 1912, ii, 696) has been applied to mercuric cyanide, but the reaction is very incomplete. C. H. D.

**Aluminium Alloys and their Analysis.** W. E. VON JONX (*Chem. Zet.*, 1913, 37, 363).—A number of aluminium alloys suffer from the disadvantage that they are attacked by sea-water. It is pointed out that in investigating the effect of sea-water it should be used in the normal condition, since in one case an alloy was hardly attacked by sea-water which had been concentrated to one-fifth of its volume, whereas it was attacked appreciably by the ordinary sea-water.

The analysis of the alloys is best carried out as follows: 1 gram of the alloy is dissolved in hydrochloric acid, the solution evaporated to dryness, and the silica estimated as usual. The lead and tin in the filtrate are estimated in the usual way; to the filtrate from these metals is added bromine water, and then alkali in excess. After heating to boiling and keeping overnight, the precipitate, which contains copper, iron, manganese, and magnesium, is collected, and these metals are estimated as usual. The zinc in the filtrate is precipitated with ammonium sulphide and weighed as sulphide, after which it is dissolved in hydrochloric acid and tested with ammonia for aluminium, which, if present, must be allowed for. The alkaline solution containing the aluminium and zinc may also be poured into acetic acid, and the zinc then precipitated as sulphide with hydrogen sulphide. The zinc sulphide is then dissolved in hydrochloric acid, the aluminium present precipitated as hydroxide, and the zinc again precipitated as phosphate.

If the alloy does not contain silica, lead, or tin, it is dissolved directly in alkali hydroxide. T. S. P.

**Alkali-Acidimetric Estimation of Alumina and the Acidimetry of the Free Acid in Aluminium Salts.** S. FISM (*Chem. Zentr.*, 1913, i, 958-959; from *Abhandl. deut. naturwiss. med. Ver. Böhmen*, 1913, iii, 213-237).—The solution of alumina in hydrochloric or sulphuric acid is roughly titrated with phenolphthalein and diluted to about 0.03N. The total acidity is estimated in one portion by adding a known excess of alkali and a clear solution is obtained in the cold, and then titrating back with hydrochloric acid in presence of barium sulphate in the warm. In another portion, the free acid is titrated with N-alkali in presence of sodium fluoride in a platinum dish. J. C. W.

[Estimation of] **Manganese in Ore, Ferromanganese, Spiegeleisen, etc.** Volhardt's Method. SIDNEY CROOK (*Chem. News*, 1913, 107, 157).—Two grams of the sample are treated with suitable acids, finally sulphating with 10 c.c. of concentrated sulphuric acid, and evaporating until fumes appear. The residue is transferred to a litre flask, which should then be half-filled with boiling water. Precipitated zinc oxide emulsion is added until all the iron is thrown down, carefully boiled, filtered, and washed well with hot water. The collected precipitate, which still contains some manganese, is transferred to the original flask, redissolved in 5–10 c.c. of concentrated sulphuric acid, and again precipitated with zinc oxide emulsion. The whole is then added to the main bulk, without filtering, cooled, and made up to a litre. An aliquot portion, equal to 0.25–0.5 gram of the sample, is pipetted into a 1500 c.c. Jena flask, made up to 600 c.c. with water, boiled, and then titrated with potassium permanganate solution (10 grams per litre) until the faint pink colour persists for several hours. In carrying out the titration, continuous and vigorous shaking of the contents of the flask, as well as repeated boiling, is necessary. Towards the end of the titration it is well to filter some of the solution through a hardened filter in order to compare its colour with that of a standard made by adding two drops (0.1 c.c.) of the permanganate solution to one litre of water. The end of the titration can then be told with accuracy.

It may be necessary to make a blank estimation, in order to correct for errors caused by the water, acid, and zinc oxide emulsion used.

T. S. P.

**Colorimetric Estimation of Small Quantities of Manganese in Water.** FRITZ HAAS (*Zeitsch. Nahr. Genussm.*, 1913, 25, 392–395).—In the method proposed, the manganese is oxidised with potassium persulphate, and the quantity of permanganate produced is ascertained by comparison with standard solutions of the latter. On hundred c.c. of the water under examination are acidified with 5 c.c. of 20% sulphuric acid, 1 gram of potassium persulphate is added, and the solution is heated until a reddish-violet coloration is obtained, or until a brown colour, due to manganese dioxide, develops. The solution is now cooled, a trace of sodium hydrogen sulphite is added, and the oxidation with persulphate is repeated. The coloration obtained is then compared with that exhibited by N.100-potassium permanganate solution. The most trustworthy results are obtained when the quantity of manganese lies between 0.05 and 1.0 mg. per litre of water. The presence of iron does not affect the results obtained by the method, and there is no necessity to remove chlorides by previous treatment with silver nitrate and nitric acid.

W. P. S.

**A Modified Bunsen Valve.** LESLIE RUSSELL MILFORD (*J. Ind. Eng. Chem.*, 1912, 4, 845–846).—A sketch of a modified Bunsen valve attachment used to close the neck of the Erlenmeyer flasks employed for the reduction of iron in the estimation of this metal;

it is made from the bulbous portion of a 10 c.c. pipette, inserted into the one-holed stopper, and fitted on the top with perforated rubber tubing, which is loosely closed with a glass plug.

F. M. G. M.

The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Pig Iron. CHEMISTS' COMMITTEE OF THE U.S. STEEL CORPORATION (*J. Ind. Eng. Chem.*, 1912, 4, 801-812) — A detailed description of the methods adopted as standards by the chemists of the U.S. Steel Corporation for the analysis of pig iron, which is divided into the following sections:

1. Sampling and the character of the sample. Two optional methods are prescribed for taking the sample: (*a*) the plate or pat test, and (*b*) the chilled mould test; the use of the water shot test is considered a violation of the standard methods. The number of samples to be taken, their preparation, with sketches of the moulds to be employed are also given.

2. Methods of analysis. Silicon may be estimated by either Drown's or Ford's hydrochloric acid methods. Sulphur, volumetrically as hydrogen sulphide by titration with iodine, or gravimetrically after oxidation to sulphate.

Phosphorus, volumetrically by either acid-alkali or potassium permanganate titrations; gravimetrically as ammonium phosphomolybdate or magnesium pyrophosphate.

Manganese, by Walter's colour comparison method; by titration with sodium arsenite, or by Ford's gravimetric method.

Total carbon, by direct combustion followed by (*a*) weighing the absorbed carbon dioxide; (*b*) titration with an alkaline hydroxide; (*c*) titration and ignition of barium carbonate; (*d*) titration of excess of barium hydroxide; or by a solution-combustion method which is described.

Graphitic carbon, by combustion of the graphitic residue, with either absorption of carbon dioxide, or by loss of weight when ignited in a crucible.

Combined carbon, indirectly from the total carbon, or by the colour comparison method.

Titanium, colorimetrically.

Copper, gravimetrically as copper oxide or volumetrically with iodine and sodium thiosulphate.

F. M. G. M.

Estimation of Iron and Titanium in Ceramic Materials. HERMOLD RUCKE and RICHARD BETZEL (*Chem. Zentr.*, 1913, 1, 656-657; from *Arch. Physik. Chem. Glas. and Ceram. Massen*, 1912, 1, 15-18). — Since not only the iron, but also the titanium present in the clay, have an influence on the firing-colour, it is advisable to estimate them both. If the iron is to be titrated by permanganate, the solution should be reduced by stannous chloride, hydrogen sulphide, or sulphur dioxide, or if reduced by zinc, the titanium present must be reoxidised by bismuth oxide. An iodometric estimation is preferable. For the titration of titanium, which is

usually present in less than 1% as dioxide, a colorimetric method requiring a special but simple apparatus is described. J. C. W.

**The Colorimetric Estimation of Iron in Lead and its Oxides.** JOHN A. SCHAEFFER (*J. Ind. Eng. Chem.*, 1912, **4**, 659-660).—A modification of the method previously described by Thomson (T., 1885, **47**, 493), and now adapted for the analysis of lead employed in the manufacture of glass and accumulators.

F. M. G. M.

**Estimation of Chromium and Vanadium in Steel.** D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1913, **4**, 825).—A modification of the method previously described (A., 1912, ii, 1100), which allows of the estimation of chromium and vanadium in the same sample of steel. The prepared solution is treated with sodium bisulphate, which oxidises the chromium, manganese, and vanadium to chromic, permanganic, and vanadic acids respectively; the permanganic acid is destroyed by boiling and manganese dioxide removed by filtration; the chromic and vanadic acids are reduced with ferrous sulphate to trivalent chromium and quadrivalent vanadium, and by subsequent treatment with potassium permanganate the vanadium only reoxidised, so that the amount of ferrous sulphate minus the permanganate employed measures the quantity of chromium.

The vanadium is again reduced with ferrous sulphate (not measured), the excess of ferrous sulphate oxidised with manganese dioxide, and the vanadium titrated.

The manganese dioxide (which must be natural or crystalline) must not be in too finely divided a condition (A., 1912, ii, 1101), but should settle perfectly in a beaker of water within fifteen seconds.

F. M. G. M.

**A New Volumetric Method for the Estimation of Tin.** WILHELM W. PATRICK and G. C. WILSSACK (*J. Ind. Eng. Chem.*, 1912, **4**, 397-399).—A sample corresponding with 0.5 (or less) of tin is placed in a 500 c.c. Erlenmeyer flask. 1.5 grams of metallic antimony added (if as much or more is not present in the alloy), and the mixture heated with 10 c.c. of concentrated sulphuric acid until solution is complete. The contents of the flask are cooled, treated with 10 c.c. of water and 60 c.c. of concentrated hydrochloric acid, followed by 40 c.c. more water.

The flask is closed with a four-holed rubber stopper fitted with (1) an inlet, (2) an outlet for carbon dioxide, (3) a tube through which the titrating solution is introduced, and (4) a glass rod to the base of which a spiral of Swedish iron is suspended by means of a fused-in platinum hook, which can be raised or lowered to the bottom of the flask as required.

Air is expelled by the passage of carbon dioxide and reduction, completed by the application of heat; the iron spiral is raised, carefully washed, and the tin rapidly titrated with standard iodine solution in the presence of starch.

The modifications necessary if the alloy contains more than 5%

of copper or lead or excess of antimony are also discussed in the original. F. M. G. M.

**Estimation of Platinum by Precipitation as Sulphide.** RUDOLF GAZE (*Chem. Zentr.*, 1913, i, 464; from *Apoth. Zeit.*, 1912, 27, 959—960).—The addition of 5—10% of mercuric chloride or oxynitrate expedites the precipitation of platinum as sulphide. The method gives good results in the estimation of platinum in organic double-salts. Barium platinicyanide may be decomposed by concentrated sulphuric acid or by strong ignition, and the residue extracted with aqua regia and precipitated as above. J. C. W.

**$\alpha$ -Nitroso- $\beta$ -naphthol as a Precipitant for Palladium.** W. SCHMIDT (*Zeitsch. anorg. Chem.*, 1913, 80, 335—336).— $\alpha$ -Nitroso- $\beta$ -naphthol gives a bulky, reddish-brown precipitate with palladium salts, but not with the other platinum metals. This reaction is perceptible with a solution containing 0.001 gram of palladium per litre. The method may be used quantitatively, as the precipitate is readily filtered, and yields the pure metal on ignition. The accuracy of the precipitation is not interfered with by the presence of platinum and rhodium. The precipitate has the composition  $(C_{10}H_6O_2N)_2Pd$ . C. H. D.

**New Method of Purification of Paraffin and Modification by its Aid of Marcusson and Meyerheim's Process for Identifying Different Paraffins by means of the Iodine Value.** CONSTANTIN I. ISTRATI and M. A. MIHAILESCU (*Bull. Acad. Sci. Roumaine*, 1912 13, 1, 91—94).—The paraffin is dissolved in boiling chloroform, then mixed with an equal bulk of boiling alcohol, and the solution allowed to cool. The solid matter which separates is filtered, and the filtrate distilled with the aid of a fractionating column in such a way that a portion of the chloroform is removed, after which, on cooling the residue in the flask again, it deposits a crystalline crop, which is removed, the filtrate being again subjected to a similar operation. In this manner a sample of white paraffin, m. p.  $58^\circ$ , was resolved into several fractions, the highest m. p. observed for any of them being  $78^\circ$ , whilst the last fraction was liquid at the ordinary temperature.

The modification of Marcusson and Meyerheim's method consists in the replacement of ether by chloroform. The paraffin is dissolved in a boiling mixture of alcohol and chloroform, the solution allowed to cool slowly, and the crystalline precipitate filtered and washed with a mixture of alcohol and chloroform, finally with pure alcohol. The filtrate is evaporated, and the residue again dissolved in alcohol chloroform. The crop which separates on cooling is removed, and the iodine value determined in the filtrate. The values obtained in this manner are rather higher than those given by the older method, a result which is attributed to the better separation of the paraffins. H. W.

**Relations between the Temperatures of the Vapour and of the Boiling Liquid in the Case of Mixtures of Hydrocarbone.** DAVID HOLDE (*Chem. Zeit.*, 1913, 37, 414—415).—The

author has distilled, in an Engler flask, crude Galician petroleum and also a refined (safety) petroleum (flash point  $56^{\circ}$ ,  $D_{4}^{20}$  0.800), measuring at the same time the temperatures of the boiling liquid and of the vapour in contact with it. In the case of the crude petroleum the temperature range of the boiling point (thermometer in vapour) was  $>240^{\circ}$ , from  $68^{\circ}$  to  $>308^{\circ}$ , and the difference in temperature between the vapour and liquid gradually increased from  $39^{\circ}$  to  $59^{\circ}$ . In the case of the refined petroleum the temperature range was  $68^{\circ}$ , from  $184^{\circ}$  to  $252^{\circ}$ , and the temperature difference gradually decreased from  $8^{\circ}$  to  $6^{\circ}$ . The fact that the temperature difference increases continually in the case of the crude petroleum may be taken as proof that decomposition occurs to some extent, the normal behaviour, as predicted by theoretical considerations, being a gradual decrease in the temperature difference, as in the case of the refined petroleum.

The results of these experiments support the method recommended by the International Petroleum Commission for the investigation of petroleum, namely, the use of an Engler flask, and measurement of the temperature of the vapour and not of the liquid.

T. S. P.

**Vapour Pressure of Naphthalene and its Estimation in the Purification of Coal Gas.** ERNEST SCHLUMBERGER (*J. Gasbeleuchtung*, 1912, 55, 1257–1269).—A description of the apparatus employed, and the method of procedure, by means of which the amount of naphthalene present in coal gas is estimated by the determination of vapour pressure. The vapour pressures corresponding with mixtures containing different proportions of coal gas and naphthalene are tabulated at temperatures (taken at intervals of 5 degrees) between  $0^{\circ}$  and  $50^{\circ}$ .

F. M. G. M.

**A New Method for the Estimation of Glycerol.** S. H. BERTRAM (*Chem. Weekblad*, 1913, 10, 237–239).—The method depends on the formation of a soluble derivative of copper and glycerol on addition of copper sulphate to an alkaline solution of glycerol at ordinary temperature. The copper is estimated by adding excess of potassium iodide to the solution containing acetic acid, and titrating back with  $N/10$ -thiosulphate. The constitution of the copper compound is unknown, but its copper content corresponds with 1 atom to 2 molecules of glycerol.

A. J. W.

**Rapid and Accurate Methods for Estimating Phenol.** L. V. REDMAN and E. O. RHODES (*J. Ind. Eng. Chem.*, 1912, 4, 655–659).—A discussion of various methods which have been employed for the estimation of phenol with a description of two (the hypobromite method and the bromide-bromate method), in the first of which the phenol is shaken with potassium hypobromite, subsequently treated with iodine, and titrated with sodium thiosulphate; the second method is similar, except that the hypobromite is replaced by a mixture of potassium bromide and bromate



(Koppeschaar's solution). The advantages claimed are, an accuracy of 0.3% with only one minute's continuous shaking.

The phenol should in each case be diluted to approximately  $N/100$  concentration, when the resulting precipitate will be white and flocculent, showing no traces of red tetrabromo-*p*-benzoquinone or of yellow tribromophenol bromide. The phenol solution must be acid after the bromine is added; if alkaline, an error (of as much as 67%) is introduced, which increases as the concentration of the phenol in the solution diminishes, and the reaction period increases.

F. M. G. M.

**The Estimation of Phenol in Crude Carboic Acid and Tar Oils.** JONX MORRIS WEISS (*J. Franklin Inst.*, 1912, 683—690).

—Eleven different mixtures containing varying proportions of *o*-, *m*-, and *p*-cresols were each treated with 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95% of phenol, and the b. p., density, and solidifying point of each mixture carefully determined. From the data (which is tabulated) it is considered possible to estimate absolute phenol in crude natural mixtures of tar oils within an error of 2.5%.

The synthetic preparation of pure phenol, and the purification of the *o*-, *m*-, and *p*-cresols employed in these tests, are described.

Various anomalies in the physical constants of some of the mixtures are recorded, but as they occur in those containing proportions not found in the crude oil, they are not considered likely to lead to inaccuracies if intelligently considered.

F. M. G. M.

**The Estimation of Eucalyptol (Cineole) in Essential Oils.** FRANCIS D. DODGE (*J. Ind. Eng. Chem.*, 1912, 4, 592).

—Eucalyptol is stable in the presence of cold potassium permanganate, whereas the terpenes and unsaturated compounds also present in essential oils are oxidised thereby to soluble products; the unattacked eucalyptol can be measured, and its purity confirmed by physical tests. About 10 c.c. of the oil are shaken at 0° with the addition of a 5% solution of potassium permanganate until reduction is complete; after allowing it to remain at 0° during twelve to eighteen hours, the precipitated manganese dioxide is dissolved with sulphurous acid (or sodium hydrogen sulphite and hydrochloric acid), water added, and the unoxidised oil separated.

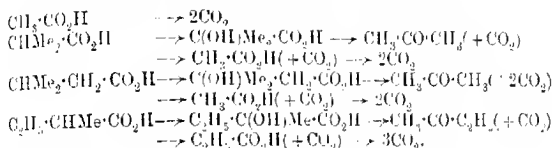
F. M. G. M.

**Estimation of Formic Acid in Foods.** HEINRICH FINGER

(*Zeitsch. Nahr. Genussm.*, 1913, 25, 386—391).—Results of estimations of formic acid by the mercuric chloride method are recorded, and the advantage of adding sodium chloride and sodium acetate to the solution before reduction are pointed out (compare A., 1911, 2, 232). Attention is drawn to the effect of the alteration of the atomic weight of mercury on the factor for calculating the quantity of formic acid from the weight of mercurous chloride. For the detection of formic acid, reduction of the acid with magnesium in the presence of hydrochloric acid is recommended, the resulting formaldehyde being detected by means of milk and hydrochloric acid containing a trace of iron.

W. P. S.

**Analysis of Mixtures of the Lower Fatty Acids.** KURT LANGFELD and ARTUR ZEILERS (*Ber.*, 1913, 46, 1171—1177).—Many physiologic-chemical investigations lead to mixtures of the lower members of different aliphatic series. As most of these substances can be easily converted into the fatty acids, an attempt has been made to solve the problem of estimating the latter in mixtures, and, in the first place, in mixtures of those acids which correspond with the most commonly occurring amino-acids, namely, acetic, *isobutyric*, *isovaleric* and  $\alpha$ -methylbutyric acids. Formic acid is omitted because it can be estimated separately. The method depends on the oxidative degradation of these acids by chromic acid. This process is well-nigh independent of concentration, but is influenced by temperature to a remarkable extent, for by regulating this, the oxidation can be stopped at different stages in exact concordance with the theoretical views represented by the equations:



At 65°, the first phase, the oxidation of secondary chains, is completed; at 100°, the oxidation of the ketones into the acids; and at 170°, the complete oxidation. Knowing the total acidity in terms of 0.1N-alkali, it is possible, by measuring the carbon dioxide evolved in these three stages, and with the aid of appropriate formulae, to estimate mixtures of these acids. The results are only approximate, but since very little substance is required, the method may be worthy of application to physiological problems. J. C. W.

**The Purine Content of Blood and Its Estimation.** R. HART BAS and WILHELM WIECHOWSKI (*Chem. Zentr.*, 1913, i, 331; from *Wiss. Klin. Woch.*, 1912, 25, 1863—1864).—Uric acid and purine bases are not precipitated from very dilute solutions by phosphotungstic acid. Such liquids as urine or blood filtrates, which contain substances which are precipitated by this reagent, may therefore be freed from those materials without loss of uric acid or purine bases, especially when precautions are taken not to add an excess of precipitant. After removing the phosphoric acid from the concentrated filtrate, silver nitrate is added, and the precipitate is decomposed by hydrogen sulphide and filtered. Uric acid crystallises out on concentrating the filtrate with hydrochloric acid, and is weighed.

Uric acid is found to be a constant constituent of human or bovine blood, but not of horse blood, whereas purine bases are common to all, but are found in largest quantity in human blood.

J. C. W.

**Detection of Uric Acid in Blood.** FRITZ OBERMAYER, ARCO POPPER, and E. ZAK (*Chem. Zentr.*, 1913, i, 658—659; from *Wien. Min. Woch.*, 1912, 25, 1967—1968. Compare preceding abstract).—The serum is freed from traces of albumin and allied substances by centrifugation with crystallised phosphotungstic acid (Merck), which does not precipitate uric acid, and then the filtrate is rendered alkaline and treated with a special phosphotungstic acid from Schuchardt, which gives a blue coloration with uric acid even in the dilution 0.01 mg. to 5 c.c. water. Other purine substances which are found in blood do not react. J. C. W.

**Behaviour of Uric Acid to Zinc Salts.** M. KASCHIMABARA (*Zeitsch. physiol. Chem.*, 1913, 84, 223—233).—On mixing solutions of zinc salts with uric acid, precipitates are obtained rich in zinc and containing small quantities of uric acid. Compounds of the two in definite proportions were not obtained.

In the quantitative estimation of uric acid in urine, slightly higher values are found using the zinc method than with the silver method. The uric acid obtained by the former method is of satisfactory purity. E. F. A.

**Colorimetric Estimation of Uric Acid in Urine.** OTTO FOLIN and WILLY DENIS (*J. Biol. Chem.*, 1913, 14, 95—100).—Full details are given of the technique in the colorimetric method introduced by Folin and Macallum (*A.*, 1912, ii, 495; this vol., ii, 80). It is possible to carry out the process in fifteen minutes. W. D. H.

**A Simple All-Glass Extraction Apparatus.** CLAYTON BEADLE and HENRY P. STEVENS (*Analyst*, 1913, 38, 143—144).—The apparatus consists essentially of an Erlenmeyer flask about three inches in diameter and 4½ inches in height to the bottom of the neck. The latter is made wide and long, 1½ to 1½ inches internal diameter, and 4½ inches long. The condenser consists of a glass vessel of test tube shape, fitted at the top with a water inlet and outlet and of about 1½ to 1½ inches external diameter, which is slipped into the neck of the flask and supported by a flange resting on the rim. The actual extraction tube consists of a glass thimble with siphon tube attached about 3 inches long, and 1 to 1½ inches external diameter. The thimble hangs by means of a flange of three or four projections at the bottom of the neck of the flask, made by softening the same and forcing a sharp-pointed instrument in to the depth of about ½ inch. The apparatus has the advantage that the substance to be extracted is immersed in the solvent or its vapour at the boiling point of the liquid. L. DE K.

**Glycerides of Fats and Oils. VI. The Theoretical Basis of Polenske's "Difference" Number.** ALFRED BOHRER and E. LINDBRICH (*Zeitsch. Natur. Genussm.*, 1913, 25, 367—386). A method proposed by Polenske (*Arbeit. Kaiserl. Gesundheits.*, 1907, 26, 144) for the detection of certain fats in other animal fats, which is based on the differences between the melting and solidifying points

of the fats, was found to be useful for the detection of tallow in lard, provided that the proportion of the former was not less than 15%. The method depends on the presence of different palmityl-diestearins in the fats; lard contains  $\alpha$ -palmityldistearin and has a "difference" number of 18.4, whilst tallow contains  $\beta$ -palmityldistearin and shows a "difference" number of 11.8. Previous crystallisation of the fats from ether does not increase the sensitivity of the method.

W. P. S.

**Analysis of Altered Milks.** L. VUAFIART (*Ann. Falsif.*, 1913, 6, 118—149).—In using the method described by Kling and Roy (*A.*, 1909, ii, 525) it is advisable to divide the sample of milk into two equal portions, one portion being reserved for analysis in case of accident to the first, or it may be employed for a duplicate estimation. The total weight of the sample is ascertained, and one-half of it is acidified with acetic acid, heated, and the coagulum separated by filtration; after being washed, the coagulum is dried at 85°, extracted successively with acetone and ether, and then mixed with the residue obtained by evaporating the serum and washings to dryness. The nitrogen is estimated in the residue by Kjeldahl's method. The author considers that milk should contain at least 29 grams of protein (nitrogen  $\times 6.39$ ) per litre, a slightly lower standard than the one suggested by Kling and Roy; the quantity of fat present should be not less than 30 grams per litre.

W. P. S.

**Estimation of Proteins in Milk (by Formaldehyde Titration).** WILLEM C. DE GRAAFF and (Mlle.) A. SCHAAP (*Ann. Falsif.*, 1913, 6, 149—157).—In the estimation of proteins by the formaldehyde process described by Steinegger (*A.*, 1906, ii, 130) the authors prefer to use sodium hydroxide solution for the titration as they find that the acidity of formaldehyde solutions does not increase with dilution when this alkali is used unless the dilution is excessive; Richmond (*A.*, 1911, ii, 236) has recommended the use of strontium hydroxide solution in order to avoid this increase of acidity. From the results obtained, the factor 0.0777 is deduced for converting the aldehyde figure into nitrogen, or 0.195 for converting it into protein; these agree with the factors given by Steinegger, but are slightly different from those found by Richmond. In the case of heated milk, the results obtained are not as concordant as those given by unheated milk. With human milk the nitrogen factor was found to be 0.0693, and the protein factor 0.443. Buttermilk yielded an aldehyde figure varying from 10.41 to 11.29.

W. P. S.

**Estimation of Sugar.** II. IVAR BANG (*Biochem. Zeitsch.*, 1913, 49, 1—18).—A modification of the author's titrimetric method for estimating sugar is described, for which at least an equal accuracy is claimed, and which has the advantage in that the standard solutions are more readily prepared and the materials required are less costly. The copper solution is made in the following way:

160 grams of potassium hydrogen carbonate, 100 grams of potassium carbonate, and 66 grams of potassium chloride are dissolved in 700 c.c. of water, the first-named substance being dissolved before the addition of the others with the aid of gentle heat ( $30^{\circ}$ ); 100 c.c. of a 4% solution of hydrated copper sulphate are then added, and the solution is diluted to 1 litre. This serves as the stock solution, of which, for sugar estimations, 300 c.c. are diluted to 1 litre with saturated potassium chloride solution. The sugar reduces the copper salt to cuprous chloride, which is kept in solution by the large excess of potassium chloride. The reduced cuprous salt present is then estimated by titration with iodine, which reacts according to the equation  $\text{CuCl} + \text{I} + \text{K}_2\text{CO}_3 = \text{CuCO}_3 + \text{KCl} + \text{KI}$ . The iodine solution required for this purpose is made by mixing 1 c.c. of 2% potassium iodate solution with 2–2.5 grams of potassium iodide and 10 c.c. *N*/10-hydrochloric acid, and diluting to 1 litre. A *N*/100-iodine solution is thus obtained. Starch solution (1% in saturated potassium chloride solution) is used as indicator. For ordinary estimations 55 c.c. of the diluted copper solution are heated for three minutes with the sugar solution, which must not contain more than 10 mg. sugar, and the mixture is then allowed to cool. Special arrangements are described for preventing oxidation during this process. The reduced copper salt is then estimated by the iodine solution; 2.70 c.c. *N*/100-iodine solution are equivalent to 1 mg. of dextrose. The sugar solution should be free from proteins and substances which are acted on by iodine; hence certain precautions are necessary in applying the method to the estimation of sugar in urines. S. B. S.

**A Method of Microchemical Estimation of Certain Constituents of the Blood.** IVAR BANG (*Biochem. Zeitsch.*, 1913, 49, 19–39).—The blood, which need not weigh more than 0.1 gram, is taken up on a weighed strip of filter paper, and then rapidly weighed on a torsion balance designed by Hartmann and Braun. The weighing can be so rapidly performed that no appreciable loss due to evaporation of moisture takes place. To estimate the sugar in this, the paper is transferred to a test-tube, to which is added 7 c.c. of a hot saturated potassium chloride solution, previously acidified by the addition of 2 or 3 drops of 40% acetic acid. The liquid is then transferred to a 50 c.c. flask, the paper is washed with 4 c.c. potassium chloride solution, and then 3 c.c. of the undiluted stock solution containing copper sulphate, potassium carbonates, and potassium chloride (preceding abstract) are then added, and with the precautions described (*loc. cit.*) the reduction is carried out. As only fractions of a mg. of sugar are present, the iodine solution (*N*/100) necessary to titrate the reduced copper is less than 1 c.c., hence a special microburette is employed. Exact details are given by the author, together with illustrations of the method of application.

A method is also given for the microchemical estimation of sodium chloride. To about 100 mg. of blood (weighed on the filter paper by the torsion balance) are added 10 c.c. of a hot

solution of magnesium sulphate containing nitric acid. After cooling, 2 c.c. of  $N/100$ -silver nitrate solution are added, and then a definite quantity of kieselguhr, without which a clear filtrate is not obtainable. The mixture is shaken and then filtered, and the precipitate is washed with water. To the filtrate is then added 2 c.c. of a solution made by dissolving 0.615 gram of potassium iodate and 1.7 gram of potassium iodide in a litre. The excess of iodide (not precipitated by the silver) is then estimated by titration from a microburette with  $N/100$ -silver nitrate solution. The silver does not react with the iodine until it has reacted with all the iodide. The titration is carried out in the presence of a few drops of starch solution indicator made by dissolving 1 gram of soluble starch in 100 c.c. of 20% potassium nitrate solution. The number of c.c. of silver solution multiplied by 0.585 gives the number of mg. of sodium chloride. A correction must be made by blank experiment for the adsorption of silver salt by the kieselguhr. Examples of the application of the method are given, and also suggestions for the microestimation of water, haemoglobin, total nitrogen, nitrogen of extractives, albumin, and globulin.

S. B. S.

**Estimation of Sugars by the Kjeldahl-Bertrand Method.** PAUL BEYER-DORFER (*Zeitsch. ges. Brauerei*, 1912, 35, 556-559, 569-572, 582-584).—A detailed account of numerous experiments on the estimation of sugars (especially in beer and worts), from which the author deduces a method combining that of Kjeldahl with that of Bertrand (A., 1907, ii, 136), in which the cuprous oxide obtained by the first process is treated with ferric sulphate, and the ferrous salt so obtained titrated with potassium permanganate.

F. M. G. M.

**Chemical Estimation of Lactose in Milk.** ROCCARDO SANFELICI (*Chem. Zentr.*, 1913, i, 566-567; from *Staz. sperim. agric. ital.*, 1912, 45, 908-916).—The following solutions are recommended for the titration of lactose: i. 1.158 grams of copper sulphate to 1 litre of water; ii. 20.4 grams of Rochelle salt, 20.4 grams of potassium hydroxide, 300 c.c. of ammonia (D 0.91), water to 1 litre. Twenty c.c. of milk are diluted with 50 c.c. of water, boiled, and treated with 5 drops of acetic acid, when the casein and fat are precipitated and the albumin coagulated. The liquid is cooled, made up to 100 c.c., filtered into a burette, and run into a boiling mixture of 10 c.c. of solutions i and ii, 20 c.c. water, and 10 c.c. concentrated ammonia. The results are usually about 0.2% higher than with Fehling's solution.

J. C. W.

**Estimation of Sugars in Foods (Honey, Confectionery, Jams etc.).** C. F. MITTELET (*Ann. Falsif.*, 1913, 6, 138-143).—Sucrose, dextrose, and levulose may be estimated in a solution by determining the cupric reducing power and the optical rotation; in calculating the quantities of the different sugars present the following constants are taken into account: sucrose has

$[\alpha]_D^{20} + 66.50^\circ$ ; dextrose,  $[\alpha]_D^{20} + 53.00^\circ$ ; levulose,  $[\alpha]_D^{20} - 93.50^\circ$ ; invert sugar,  $[\alpha]_D^{20} - 20.25^\circ$ . The sugars in from 5 to 10 grams of the material under examination are obtained in 100 c.c. of solution, after the removal of other reducing and optically active substances, and the reducing power of this solution is determined both before and after inversion, the results being expressed as grams of invert sugar per 100 c.c. of solution; let these quantities be  $p$  and  $q$  respectively. The rotation of the solution is also determined at  $20^\circ$  in a 200 mm. tube. The amounts of the different sugars per 100 c.c. are then calculated from the equations: Sucrose  $= 0.95(q - p)$ ; dextrose  $= p - L$  ( $L$ —grams of levulose); levulose  $= (1.06 \times p) - d$ . In the last equation,  $d = D - c$ , where  $D$  is the

rotation observed and  $c$  the rotation due to the amount of sucrose present ( $c = \text{sucrose} \times 1.33$ ). The quantities of sugars found are, finally, calculated into percentages of the original substance.

W. P. S.

**Inversion of Raw Sugar Solutions with Ammonium Chloride.** FRIEDRICH STROHMER and OTTOKAR FALLADA (*Osterr.-ung. Zeitsch. f. Zucker-Ind. u. Landw.*, 1912, **41**, 932—938).—A further account of the method (*Proc. 8th Internat. Cong. Appl. Chem.*, 1912) in which the author employs ammonium chloride for inversion when estimating sugar in unpurified solutions. F. M. G. M.

**Estimation of Starch and Dextrin in Sugar Products, Confectionery, etc.** A. AUGER (*Ann. Pâtis.*, 1913, **6**, 143—147).—In the method proposed, 0.5 gram of the substance is inverted by heating at  $70^\circ$  with 1% hydrochloric acid, and the reducing sugars are then estimated by titration with Fehling's solution in the usual way. Another portion of 0.5 gram of the sample is inverted by heating it with 2% hydrochloric acid for one hour at  $110^\circ$ , and the reducing sugars now present are estimated. The difference between the two estimations, expressed in terms of invert sugar, is multiplied by 0.9 to give the quantity of starch or dextrin. A preliminary examination of the substance under the microscope, and a test with iodine solution, will show whether starch or dextrin is present, or which of these preponderates.

W. P. S.

**Difficulties in the Colorimetric Estimation of Vanillin.** W. S. HERBERT (*J. Ind. Eng. Chem.*, 1912, **4**, 669—670).—The American official method (Bureau of Chemistry) of estimating vanillin colorimetrically with bromine water and ferrous sulphate is considered to have the following disadvantages:

(1) A difficulty in getting the maximum coloration: the original method of adding the ferrous sulphate first gives a deeper colour than the present one, where the bromine is added first.

(2) It is difficult to add only enough lead cream to decolorise the solution, and when different quantities are added, the depth of colour subsequently obtained varies.

(3) Dilution of the sample influences the colour.

- (4) Much larger amounts of ferrous sulphate are necessary in comparison with bromine water to produce a maximum colour.
- (5) Lead cream forms a yellow, crystalline lead vanillin derivative,  $(C_8H_7O_2)_2Pb$ , which renders a quantitative estimation impossible in the presence of lead.
- (6) It seems possible that vanillin is oxidised to pyrocatechuic acid.

F. M. G. M.

**A New Colorimetric Method for the Determination of Vanillin in Flavouring Extracts.** OTTO FOLIN and WILLEY DENIS (*J. Ind. Eng. Chem.*, 1912, 4, 670-672).—The Winton method (A., 1905, ii, 620) for estimating vanillin, although accurate, is somewhat lengthy, and the following colorimetric method has now been employed. The recently described phosphotungstic-phosphomolybdic acid reagent (A., 1912, ii, 1011), when added to an acid solution of vanillin, gives, on addition of sodium carbonate a rich blue colour. The vanillin extract (5 c.c.) is treated with 75 c.c. cold water and 4 c.c. of a solution of lead acetate; the volume made up to 100 c.c., the solution filtered, and a measured quantity of the filtrate shaken with 5 c.c. of the reagent, and after five minutes made up to a known volume with a saturated solution of sodium carbonate. After filtration, the resulting dark blue liquid is compared in a Duboseq colorimeter with a similarly treated standard vanillin solution.

F. M. G. M.

**Estimation of Acetone in Urine.** O. SAMMET (*Zeitsch. physiol. Chem.*, 1913, 83, 212-225).—Various methods for the estimation of acetone have been submitted to critical examination, particular attention being paid to the application of the methods to the estimation of acetone in urine. Graaf's *p*-nitrophenylhydrazone method (A., 1907, ii, 588) was found to yield from 95.5 to 96.2% of the quantity of acetone actually present when the amount of acetone varied from 0.1 to 0.2 gram per 100 c.c. of urine. Messinger's method (compare A., 1908, ii, 234) also yielded trustworthy results. When this method is used for the estimation of acetone in urine, the latter should be treated with tartaric acid and distilled; calcium carbonate is then added to the distillate, and the mixture again distilled. The second distillate is rendered alkaline with potassium hydroxide solution, an excess of *N*/10-iodine solution is added, and, after shaking, the mixture is acidified with hydrochloric acid, and the excess of iodine is titrated with thio-sulphate solution. Each c.c. of *N*/10-iodine solution is equivalent to 0.000967 gram of acetone. The yield obtained by the method was about 96% of the quantity of acetone present. Oppenheimer has employed a method proposed originally by Dengès (A., 1899, i, 475), but the author finds that the results obtained are about 10% too high when Oppenheimer's factor (0.055) is used for converting the weight of the precipitate into acetone; better results are obtained when the factor 0.0195 is employed. The volumetric method of estimating the mercury in the precipitate is untrustworthy. The author has also attempted to estimate the amount of

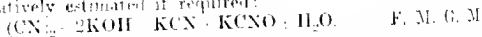


acetone from the volume of the precipitate obtained in Denigès' method; the precipitate was subjected to centrifugal action until it ceased to decrease in volume, and it was found that the volume of the precipitate multiplied by 0.0912 gave the weight of acetone. This is only the case when the volume of the precipitate does not exceed 0.4 c.c., and even then the results obtained are not strictly concordant. W. P. S.

**Estimation of Acetone Substances in Blood and Tissues by Micro methods.** W. McKIM MARRIOTT (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxvii; *J. Biol. Chem.*, 14).—Acetone, acetoacetic acid, and  $\beta$ -hydroxybutyric acid may be estimated in 2 to 5 c.c. of blood. Acetone is distilled off and estimated by the turbidity it occasions in an alkaline mercury silver cyanide solution by the nephelometer;  $\beta$ -hydroxybutyric acid is estimated by oxidation to acetone after removal of proteins and sugar. W. D. H.

**Applied Plant Microchemistry. VII. Microchemistry and Microsublimation of Some Methane Derivatives.** OTTO TUXMANN (*Chem. Zentr.*, 1913, i, 192; from *Apoth. Zeit.*, 1912, 27, 971-974, 983-985).—Diagrams are given showing the different sublimation forms of hydroxymethylanthraquinone from rhubarb root, mannitol from manna, *Olea europaea* and *Fraxinus ornus*, maleic acid and its anhydride from *Sorbus aucuparia* and *Euphorbia*, citraconic acid and its anhydride from the citric acid of *Citrus*, sorbic acid from *Sorbus aucuparia*, and fatty acid crystals with their myelin forms from *Arca catechu*, *Allicium religiosum*, and *Elaeis guineensis*. J. C. W.

**The Detection and Estimation of Cyanogen and Hydrogen Cyanide.** F. H. RHODES (*J. Ind. Eng. Chem.*, 1912, 4, 652-653).—Two absorption tubes, the first containing 10 c.c. of a 10% solution of silver nitrate and one drop of N. G. nitric acid, and the second, 10 c.c. of N. 2-potassium hydroxide, are connected, and the gaseous mixture of cyanogen and hydrogen cyanide passed through them, followed by a slow current of air for about ten minutes. The tube containing potassium hydroxide is then disconnected, treated with 5 c.c. of a solution of ferrous sulphate and one drop of a solution of ferric chloride; after about fifteen minutes the precipitated ferro-ferric hydroxides are dissolved with dilute sulphuric acid, when the appearance of a distinct green colour, or of a blue precipitate, proves the presence of cyanogen in the original gas. The hydrogen cyanide is quantitatively absorbed by the silver nitrate, whilst the cyanogen is converted by the potassium hydroxide into potassium cyanide and potassium cyanate, which can be quantitatively estimated if required:



**Estimation of Creatine and Creatinine in Diabetic Urines.** ISIDOR GREENWALD (*J. Biol. Chem.*, 1913, 14, 87-91).—In urines containing acetoacetic acid or acetone, creatinine may be estimated

accurately by Folin's method only after these substances are removed. Dextrose in concentrations up to 5% has no appreciable effect on the estimation of creatine by the Folin method.

W. D. H.

**The Colour Reactions of Certain Indole Derivatives and their Significance with Regard to the Glyoxylic Reaction.** (Miss) ANNE HOMER (*Biochem. J.*, 1913, 7, 116-126).—The formation of coloured condensation products from indole derivatives and certain aldehydes necessitates the use of condensing agents. The reaction takes place between the  $\cdot\text{NH}$  group of the indole nucleus and the  $\cdot\text{CHO}$  group of the aldehyde. The evidence adduced confirms the view originally advanced by Rosenheim that the Adamkiewicz reaction is primarily a formaldehyde reaction. In Hopkins and Cole's modification of the test, glyoxylic acid reacts by virtue of its decomposition into formaldehyde; the latter is in a nascent state, and therefore more reactive.

W. D. H.

**Some Colorimetric Estimations; Rowntree and Geraghty's Method for Diagnosing the Kidneys; the Estimation of Thiocyanates in Saliva and of Iodine in Urine.** WILHELM AUTENRIETH and ALBERT FUNK (*Chem. Zentr.*, 1913, i, 661; from *München. med. Wuch.*, 1912, 59, 2657-2660, 2736-2739).—Rowntree and Geraghty's method for observing the functions of the kidneys (*J. Pharm. exper. Ther.*, 1910, 1, 519) depends on the injection of phenolsulphonephthalein and its detection in the urine by means of the red colour produced by alkalis. For quantitative purposes, Autenrieth and Koenigsberger's colorimeter is recommended. A normal kidney excretes 15-60% of the reagent during the first hour after intramuscular injection, and 70-90% by the end of two hours; a kidney which excretes less than 45% is unhealthy.

The same apparatus may be applied to the estimation of thiocyanates in saliva; 0.1 to 1.0 mg. KCNS in 10 c.c. of solution may be estimated.

The colorimetric estimation of iodine in urine is very exact, since iodine may be completely extracted by chloroform, and the solution is easily standardised. If the iodine is present in ionic combination, it is liberated by sodium nitrite, but if not, the urine must be evaporated and the iodine set free from the ash.

J. C. W.

**Estimation of Pepsin.** STEFAN VON DOGÁNDY (*Zeitsch. physiol. Chem.*, 1913, 84, 18-28).—The principle involved consists in precipitating the unchanged casein after digestion with pepsin for a stated time and the determination of the optical rotatory power of the filtrate. The precipitating reagent contains 150 grams of sodium sulphate, 50 grams of magnesium sulphate, and 100 c.c. of 96% alcohol in 1000 c.c.; 60 c.c. of a 3% casein solution containing 5.5 c.c. of normal hydrochloric acid per 100 c.c. are digested with pepsin at 40°, 30 c.c. of the precipitating reagent are added, and the volume made up to 100 c.c.; the contents of the vessel are well

shaken and filtered, and the clear liquid examined in the polarimeter.

The method is applied to determining the influence of varying the time, amount of enzyme or substrate, and the amount of acid on the velocity constants of the reaction calculated from the expressions of Schütz and of Arrhenius. The results confirm those obtained by the alternative methods, to which the new method is to be preferred on account of its simplicity and accuracy. E. F. A.

**New Reagent for Detecting Blood.** ROBERT F. RUTAN and R. H. M. HARDISTY (*The Canadian Med. Assoc. J.*, Nov., 1912, Reprint. 4 pp.).—A 4% solution of toluidine in glacial acetic acid is recommended for the detection of small quantities of blood. One c.c. of the liquid to be tested for blood is treated with 1 c.c. of 3% hydrogen peroxide and 1 c.c. of the reagent; if blood is present a green to bluish-black coloration develops gradually and persists for several hours. The reagent was found to be capable of detecting 1 part of blood in 7,000,000 parts of aqueous solution, 1 in 24,000 parts of urine, 1 in 100,000 parts of feces, or 1 in 30,000 parts of stomach-contents; it is more sensitive than the similar benzidine reagent (A., 1911, ii, 318). W. P. S.

**Application of the Ammonium Carbonate Method for the Estimation of Humus in Hawaiian Soils.** J. B. RATHER (*J. Ind. Eng. Chem.*, 1913, 5, 222—223).—The ammonium carbonate method (compare *ibid.*, 1911, 3, 660) for the estimation of humus in soils, has given uniformly good results on a number of the soil types of the United States, but on exceptional soils, such as those of Hawaii, it must be modified, as follows, in order to remove the clay. The solution is prepared according to the official method, except that it is decanted instead of being filtered; 100 c.c. are placed in a graduated flask, 2 grams of ammonium carbonate added, and the whole heated for an hour on the steam-bath. After keeping overnight, 50 c.c. of the supernatant solution are pipetted off and evaporated to dryness in a tared dish; dried for three hours at 100°, weighed, ignited, and weighed again. The loss in weight represents the humus. T. S. P.

**Estimation of Colloids in Effluents containing Sugar.** PAUL ROULAND and V. MEYSAHN (*Zetsch. Ver. deut. Zuckerind.*, 1913, 167—168).—One hundred c.c. of the neutral effluent free from suspended matters are treated with 1 c.c. of a 1% aniline-blue solution, and then evaporated to a syrupy consistence. This is mixed with hot water, and the insoluble, coloured residue is collected on a weighed filter, washed with hot water, dried, and weighed. The excess of aniline-blue is estimated colorimetrically in the filtrate, thus giving the weight of the dye contained in combination with the colloids in the insoluble residue; on subtracting the weight of the dye from that of the total precipitate, the weight of colloid is found. W. P. S.

## General and Physical Chemistry.

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**Determination of the Refractive Indices of Gases under High Pressures. II. The Dispersion of Air and Carbon Dioxide.** LODEWYK H. SIERTSEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 925—931. Compare A., 1912, ii, 213).—The author has measured the refractive index of air at pressures varying from 30 to 100 atmospheres, and of carbon dioxide at pressures between 20 and 47 atmospheres. The observations were made with light of wave-length ranging from  $\lambda = 405$  to  $\lambda = 644\mu$ . The results show that in both cases the dispersion constants are independent of the pressure within the limits of experimental error. The values of the constants are compared with those obtained by previous observers.

H. M. D.

**Further Remarks on a Formula for the Index of Refraction of Binary Mixtures.** FRÉDÉRIC SCHWERS (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 447—452).—A reply to the criticism of Mazzucchelli (this vol., ii, 165).

R. V. S.

**Iridescent Layers of Gelatin and their Employment in the Manufacture of Artificial Pearls.** RAPHAEL E. LIESEGANG (*Zellulosechem. Ind. Kolloide*, 1913, **12**, 181—188).—The author has made experiments on the nature of the iridescent films which are obtained when a solidified gelatin solution of a calcium salt is allowed to interact with a solution of an alkali phosphate. To obtain these films, a drop of calcium nitrate solution is added to 5 c.c. of a 10% solution of gelatin, which is spread on a glass plate and allowed to solidify; a solution of trisodium phosphate is then brought into contact with the layer of gelatin, and the plates are left undisturbed for some hours. The iridescence appears to be due to the precipitation of calcium phosphate in the form of a more or less regular succession of layers of precipitate, which give rise to a grating-like structure.

The conditions under which this diffusion effect may be utilised for the production of "artificial pearls" are discussed. The iridescent gelatin films may be hardened by the action of formaldehyde vapour.

H. M. D.

**Dispersion of Metals.** LYNDE P. WHEELER (*Phil. Mag.*, 1913, [vi], **25**, 661—679; *Amer. J. Sci.*, 1913, [iv], **35**, 491—508).—From an examination of the available data for the dispersion of silver, copper, gold, nickel, and cobalt, it is found that the results obtained by different observers differ in general by an amount which is considerably greater than the errors inherent in the methods of measurement employed.

From a comparison of the data with the dispersion formula derived from the electron theory, it appears that the number of

free electrons is not constant, but increases with the frequency of the currents set up by the incident radiation. The rate of increase is relatively small in the infra-red, but is much greater in the regions where the metals are more transparent.

It is also shown that the dispersion of the dielectric constant can be calculated from the optical constants for the above metals. The value of the dielectric constant at any wave-length is resolvable into two parts, which may be distinguished as the "dielectric" and "conductor" parts. The latter, which depends on the presence of free electrons, is more important than the pure dielectric term, especially at the shorter wave-lengths. In general, the form of the dispersion curves is not inconsistent with that indicated by theory, but the experimental data are scarcely accurate enough to test the point satisfactorily.

H. M. H.

**Absorption of Light by Inorganic Salts. VII. Aqueous Solutions of Iron Salts.** JOHN S. ANDERSON (*Proc. Roy. Soc. Edin.*, 1913, 33, 35—43. Compare A., 1911, ii, 785, 786; 1912, ii, 595, 596). The apparatus employed for the measurements was the same as that described in previous papers. The salts examined were ferric chloride, bromide, nitrate, and sulphate, and ferrous chloride and sulphate. Observations were made over the region extending from  $\lambda = 434\mu\mu$  to  $\lambda = 1300\mu\mu$ , and curves are plotted from the results which show the variation of the molecular extinction coefficient with the wave-length of the absorbed rays, and also the influence of the concentration of the dissolved salt on the absorption.

For the chloride, nitrate, and sulphate, the infrared band increases in height, and the maximum point of the band shifts towards the visible region on dilution, whereas with ferric bromide the height of the band decreases with dilution, although the shift is in the same direction as for the other ferric salts. The infrared band of ferrous chloride shows but little alteration when the concentration of the solution is varied.

The absorption in the visible spectrum increases with dilution in the case of ferric nitrate and sulphate, but decreases with dilution for the bromide. For the chloride the absorption decreases at first with dilution, and then increases to a slight extent. This is suggested to be due to the formation of colloidal hydroxide. The absorption of freshly prepared solutions of the ferric salts differs quite appreciably from that of solutions which have been prepared for some time.

H. M. H.

**Absorption of Light by Inorganic Salts. VIII. Alcoholic Solutions of Copper, Cobalt, and Nickel Salts in the Ultra violet.** ALEXANDER R. BROWN (*Proc. Roy. Soc. Edin.*, 1913, 33, 44—48. Compare preceding abstract). The salts examined were the chlorides and bromides, and in the case of copper, the sulphate, observations being made over the region  $\lambda = 265\mu\mu$  to  $\lambda = 750\mu\mu$ . The calculated molecular extinction coefficients are plotted against the wave-lengths, and the resulting curves are compared. The

nickel salts afford evidence of a new absorption band with its maximum at about  $\lambda = 410\mu\mu$ . H. M. D.

**Absorption of the Ultra-violet Rays by Ketones, Diketones, and Ketonic Acids.** JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, 156, 1322—1324. Compare this vol., ii, 263).—The authors have determined the molecular coefficients of absorption and the positions of maximum and minimum absorption of a number of aliphatic ketones and diketones and ketonic acids, and from their results have drawn the following conclusions. All substances having the general formula,  $C_nH_{2n+1}\cdot CO\cdot C_mH_{2m+1}$ , have an absorption band between  $\lambda = 2700$  and  $2800$ , the position and height of the band varying but little with  $m$  and  $n$ . For the homologues above methyl ethyl ketone, a minimum absorption is often noticeable at  $\lambda 2100$ . The method of linking in the alkyl radicals and the position of the ketonic group have a marked effect on the value of the coefficient of absorption. The introduction of a second ketone group into the molecule increases the absorption, without altering the position of the maximum. The introduction of the carboxyl group into a ketone has a double effect in that the absorption due to the carboxyl group is increased, whilst that of the ketone group is diminished. Where a substance can exist in both the enolic and the ketonic form, the absorption varies considerably with the proportion of each form present. Methyl and ethyl acetoacetate exhibit a somewhat unusual absorption band in the region  $\lambda = 2400$ . W. G.

**A Fluorescence Spectrum of Iodine Vapour.** JOHN C. McLENNAN (*Proc. Roy. Soc.*, 1913, A, 88, 289—296).—An apparatus is described by means of which it has been possible to subject iodine vapour to intense illumination by light of wave-length extending from beyond  $\lambda = 700\mu\mu$  down to  $\lambda = 18\mu\mu$ . The apparatus consists of an outer glass illuminating tube of the ordinary Cooper-Hewitt type, and an inner tube of clear fused quartz, which is sealed into the former by wax joints. The outer tube is furnished with mercury electrodes, and carries the mercury arc, whilst the inner tube, after the introduction of crystals of iodine, is exhausted and sealed off.

The fluorescence spectrum, which is exhibited by the iodine vapour under these conditions, is characterised by the presence of a large number of narrow bands extending from about  $\lambda = 460$  to about  $\lambda = 210\mu\mu$ . More than eighty such bands have been recognised on the photographic records, and the mean wave-lengths of these are recorded.

When the inner quartz tube is replaced by a similar tube of glass, the band spectrum disappears. From this it is inferred that the emission of the banded spectrum is not due to the elevated temperature of the iodine vapour in the tube, but is a true resonance or fluorescence effect. The fact that the glass tube inhibits the banded spectrum indicates further that the exciting light consists of short-waved rays, which are absorbed by the walls of the glass tube.

The spectrum investigated by the author shows none of the lines

belonging to the fluorescence spectrum of iodine vapour examined by Wood (compare A., 1911, ii, 83, 170, 950; A., 1912, ii, 1918). The absence of these lines is probably due to the existence of a very considerable temperature gradient in the iodine vapour. In these circumstances, the light which constitutes the spectrum excited by the green and yellow mercury lines has to pass through a considerable column of cool iodine vapour, which causes the absorption of the fluorescence lines.

H. M. D.

**The Relationship between Fluorescence and Chemical Constitution.** JOHANNES STARK (*Zeit.-ch. Elektrochem.*, 1913, 19, 337—401).—Polematic. An answer to Liebig's criticism (this vol., ii, 170) of Stark's theory of fluorescence (this vol., ii, 2). Stark briefly reiterates the main points of his theory, and points out reasons why fluorescence has not been observed in so large a number of organic compounds. He points out that Liebig's view, that the fluorescence of acetone, diacetyl, etc., is due to their decomposition by the light employed in the experiments, is not in accordance with experimental facts. These substances show the fluorescence instantaneously and at its maximum intensity as soon as the light is brought to bear on them, and do not slowly grow in intensity as would be required if Liebig's view were correct.

J. F. S.

**Photoelectric Investigation of Fluorescent Substances** WILHELM E. PAULI (*Ann. Physik.*, 1913, [iv], 40, 677—700).—A number of fluorescent substances have been examined with respect to their photoelectric activity in order to ascertain whether there is any connexion between the two effects. The substances chiefly examined were anthracene, 2:5-dimethoxybenzylideneindanone, *m*-aminocyanostilbene, and 2:5-dimethoxycyanostilbene, all of which are excited to maximum fluorescent activity by light in the visible region. In regard to their photoelectric properties, it was found that none of these substances is excited to measurable photoelectric activity by light of wave-length greater than  $\lambda = 4200\text{m}\mu$ , although they all become active when subjected to the influence of ultra-violet rays. If the distribution curves showing the influence of the wave-length of the exciting light on the fluorescent and photoelectric effects are compared, it is evident that the two phenomena are not genetically related. The results are discussed with reference to the explanation of the fluorescence and photoelectric emission effects in terms of the electron theory.

H. M. D.

**The Various Photoelectric Effects shown by Anthracene, their Relations to One Another and to the Fluorescence and the Formation of Dianthracene.** MAX VOLMER (*Ann. Physik.*, 1913, [iv], 40, 775—796).—From an investigation of the photoelectric properties of solutions of anthracene in carefully purified hexane, it has been found that the Hallwachs effect is not produced by light of that range of wave-lengths which gives rise to fluorescence and to polymerisation of the anthracene, that is, by light extending from  $\lambda = 400$  to  $\lambda = 225\text{m}\mu$ . With shorter waved rays, the Hallwachs effect can, however, be readily detected.

The longer-waved rays referred to give rise to a different type of photoelectric effect, which consists in the decomposition of the solid anthracene with the formation of ions, which are sent off by the layer of anthracene on the illuminated electrode under the influence of the applied electric field. According to whether the electrode is positively or negatively charged, the emitted ions are positive or negative. A similar effect is found in the case of solutions of sulphur in hexane, except that in this case the effect is unipolar, and the photoelectric ionic emission appears to be confined to positively charged ions.

It has been further shown that hexane solutions of anthracene increase in electrical conducting power to a large extent when subjected to the influence of ultra-violet rays of wave-length less than  $\lambda = 225\mu$ . This alteration in the conductivity appears to be due to ionisation in the solution, and is attributed to the emission of electrons by the dissolved molecules under the influence of the short-waved rays.

The observations are discussed in reference to Stark's theory of fluorescence and to the nature of the process which yields dianthracene. In particular it is shown that Byk's theory of the polymerisation process, in so far as this assumes that the primary stage consists in the emission of electrons, is inconsistent with the author's observations.

H. M. D.

**An Electrically Heated Contrivance Attached to the Polarimeter for Determining Rotatory Powers at a Constant Temperature.** EMIL AUERHALDEN (*Zeitsch. physiol. Chem.*, 1913, 84, 300—304).—An apparatus is described and figured to take six polarimeter tubes 2.5 cm. in length, of 2 c.c. capacity, in which the tubes are placed and heated electrically to a constant temperature. By rotating a screw, the tubes are brought one after the other into the field of vision and observed.

E. F. A.

**Optical Observation Tubes (Polarimeter Tubes).** SIGMUND NEUMANN (*Chem. Zeit.*, 1913, 37, 520—521).—When a glass polarimeter tube gets broken there is often a difficulty in fitting the metal end pieces and caps to a new tube, owing to the want of an exact fit. This difficulty is obviated if each end of the tube is made conical in shape, or perhaps it is better to say, funnel-shaped. A metal ring, made in two halves, and screwed on the outside, is made to fit the cone, and is kept in position by a narrow ring screwing on to it. The end piece, containing the cover glass, then screws on to the metal ring. Owing to the conical shape, it is not necessary for the tube and ring to fit exactly, the desired tight joint being made by means of, for example, a wrapping with the insulation ribbon used by the electrician. The fittings need not necessarily be of metal; ebonite, or a combination of ebonite and metal, may be used. The conical end pieces have the further advantage that small air bubbles may be collected in them without interfering with the light or vision through the tube.

T. S. P.



**Measurements on the Ultra-violet Magnetic Rotation in Gases.** J. F. SIRKS (*Physikal. Zeitsch.*, 1913, 14, 336—343).—The magnetic rotation of the plane of polarisation of ultra-violet rays of different wave-lengths has been examined in experiments with oxygen, hydrogen, and carbon dioxide. In the case of oxygen the measurements of the rotation extend to  $\lambda=265\cdot4$ , of hydrogen to  $\lambda=237\cdot8$ , and of carbon dioxide to  $\lambda=248\cdot2\mu$ . The rotation increases rapidly as the wave-length of the ultra-violet light diminishes, and the values for the different gases appear to fit satisfactorily with the data obtained by Siertsema for the rotation of rays in the visible spectrum. By combining the two series of results, and plotting the rotation (relative to the rotation for the yellow mercury line) as ordinate against wave-length as abscissa, it is shown that continuous curves are obtained in the case of each of the three gases. The curve for oxygen is much lower than the curves for the two other gases, and of these the hydrogen curve is the higher.

The observed magnetic rotation of ultra-violet rays in hydrogen is shown to be at variance with the assumption that the action of the molecules on the ultra-violet light can be referred to a single type of electron, for which  $e/m$  is constant. H. M. D.

**The Dissociation of Gaseous Compounds by Light.** Gaseous Hydrogen Compounds of the Nitrogen and Carbon Groups. Different Gases. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 156, 1243—1245. Compare this vol., ii, 365).—The rule that, for the hydrogen compounds of elements of the same group, the stability with respect to light diminishes as the atomic weight increases, holds good in the case of the nitrogen and carbon groups. Zinc ethyl is rapidly decomposed by the light from a mercury-quartz lamp. Carbonyl chloride is slowly decomposed by the extreme ultra-violet rays, whilst sulphur hexafluoride is unaffected by the light from a mercury lamp. W. G.

**A Simple Method for the Absolute Measurement [of the Energy] of Ultra-violet and Visible Light Rays.** CHRISTIAN WINTNER (*Zeitsch. Elektrochem.*, 1913, 19, 389—397).—An instrument is described, termed a fluorometer, by means of which the energy of a ray of given wave-length can be measured irrespective of the presence of ultra-red rays. The principle involved consists in allowing a beam of light from a normal lamp, after passing through light filters, to enter a rectangular quartz vessel, which is filled with a fluorescent material. In this way a narrow, fluorescent beam is produced in the quartz vessel. A second beam is produced parallel with and a few millimetres removed from the first beam, by the light under investigation. This second beam enters at the opposite side of the vessel. By means of a lens and cross wire moving over a graduated scale, the position of equal brightness is measured. From this value, by means of the expression  $\log i/L_0 = (m - m_0)(d_2 - d_1)$ , where  $i_0$  and  $L_0$  represent the light quantities in the two cases,  $m$  and  $m_0$  the extinction coefficients of

the two rays, and  $d_2$  and  $d_1$  the lengths of the two fluorescent beams at which equal brightness is obtained. The method of determining the energy quantity from these results is fully explained, together with possible errors and precautions necessary in using the method. The fluorescent solutions employed by the author are: (1) Rhodamine-B, made up of 0.004 gram per litre, useful for wavelengths 600 to 460 $\mu\mu$ , and can also be used for the ultra-violet from 340 $\mu\mu$  and downwards. (2) Sodium fluorescein, made up of 0.01 gram per litre + 2.50 c.c. of N-sodium hydroxide, useful for wavelengths from 520 $\mu\mu$  down to 254 $\mu\mu$ . (3) Quinine sulphate, made up of 0.1 gram per litre + 4 c.c. N-sulphuric acid, useful down to 260 $\mu\mu$ . In addition to its uses for the measurement of energy values, this instrument is shown to be serviceable in measuring absorption curves, and also the reaction velocities of light-sensitive and non-sensitive systems. A number of light filters for various regions are described, and a criticism of many of the older light filters is given.

J. F. S.

**A Quantitative Study of Some Photochemical Effects Produced by Ultra-violet Light.** J. HOWARD MATHEWS and LEON H. DUWEY (*J. Physical Chem.*, 1913, 17, 211—218).—Various solutions of 0.1N strength were exposed at 25° in a quartz flask to a Cooper Hewitt quartz mercury vapour lamp at 10 cm. distance. Under these conditions oxalic acid is very slightly affected, but in presence of uranium nitrate, sulphate or acetate is rapidly oxidised at a linear rate proportional to the uranium concentration. It is deduced that the decomposing action of ultra-violet light is dependent on the amount of light photochemically absorbed.

Potassium permanganate and dichromate solutions are very stable towards ultra-violet light, but the oxidation of sodium sulphite in contact with air is accelerated thereby.

R. J. C.

**The Photosensitiveness of Fehling's Solution.** ALAN LEIGHTON (*J. Physical Chem.*, 1913, 17, 205—210).—According to Byk (A., 1905, ii, 70), Fehling's solution is decomposed by light of wavelengths less than 400 $\mu\mu$ , corresponding with an absorption band in the ultra violet, whereas the red and yellow waves of the visible absorption bands have no action. This is contrary to the rule that radiations which are absorbed by a substance tend to destroy it.

It is suggested that the red light absorbed by Fehling's solution is not active enough to produce decomposition unaided, whereas in presence of a suitable reducing agent its activity might be sufficiently reinforced for it to do so. In accordance with this suggestion, the author finds that in presence of quinal within certain very narrow limits of concentration, Fehling's solution is reduced by red light, but is stable in the dark.

R. J. C.

**Phototropic Phenomena with Stilbene Derivatives.** HANS STROBE and HEINRICH MALLISON (*Ber.*, 1913, 46, 1226—1238).—It has been discovered that a small class of compounds, of which

*p*-diacetyldiaminostilbene-*o*-disulphonic acid is typical, exhibits phototropy; the substance mentioned, when exposed to direct sunlight for a few minutes, changes from bright yellow to reddish-brown, and reassumes its original colour when kept in the dark; the salts of the substance behave in a similar manner, the only variation being in the colours. The most effective light rays are included between  $\lambda 490$  and  $271\mu$ , and, indeed, this group of rays exerts a much more marked effect than the beam of light from which it is selected, because yellow and red rays accelerate the reverse change, thus favouring the restoration of the substance to the original form. Experiments with the sodium salt of diacetyldiaminostilbenedisulphonic acid show that rise in temperature has much less effect on the direct change than on the reverse, so that with an increase in temperature the illumination to produce a constant effect must be greater. It is also discovered that the presence of oxygen is necessary to the effect of light on the substance and its salts, and the application of paper soaked with an alcoholic solution of tetramethyldiaminodiphenylmethane (Arnold and Mentzel, A., 1902, ii, 352) proves the simultaneous formation of a little ozone. A photographic plate failed to detect any luminescence during the reversion of the "excited" substance to its original condition.

An examination of a number of derivatives shows that, although many give an irreversible colour change, phototropy occurs only with those which, in addition to the ethylenic linking, contain the sulphonic acid group, together with the formyl or acetyl radicals.

It remains undecided whether the oxygen exerts a mere catalytic effect, or acts by addition and elimination, but assuming the latter view, explanations are tentatively proposed as to the possible mechanism of the change.

D. F. T.

**Quantitative Relation between the Range of the  $\alpha$  Particles and the Number of Changes Emitted During Disintegration.** A. VAN DER BROEK (*Phil. Mag.*, 1913, [vi], 25, 740—742).—Only the charges carried by the  $\alpha$  particles are considered, those carried by the  $\beta$  particles being apparently neglected. The following relations seem to exist:  $\log V_a = A + nB$ , and  $\log \lambda = C + nD$ , where  $V_a$  is the velocity of the  $\alpha$  ray,  $n$  the number of charges expelled from the commencement of the disintegration series,  $B$  and  $D$  general constants, and  $A$  and  $C$  special constants for each series. F. S.

**Magnetic Spectrum of the  $\beta$ -Rays of Radioactinium and its Disintegration Products.** OTTO VON BAETTER, OTTO HAHN, and LIESE MEITNER (*Physikal. Zeitsch.*, 1913, 14, 321—323).—The radioactinium, which had accumulated in an actinium solution after keeping for some weeks, was precipitated by ammonium thiosulphate after the addition of a small quantity of zirconium nitrate. This was purified by a second precipitation, dissolved in dilute hydrochloric acid with the addition of a drop of dilute nitric acid, and the boiling solution electrolysed with a silver wire as cathode. In this way a thin layer of radioactinium was obtained, which was employed for

the photographic investigation of the magnetic spectrum. The photograph obtained by exposure of the plate for nine hours to the action of the freshly prepared substance affords evidence of the emission of  $\beta$ -rays with velocities equal to 0.73, 0.67, 0.60, 0.53, 0.49, 0.43, and 0.38 of the velocity of light. At the end of ten days a further photograph was taken of the magnetic spectrum, which showed the emission of  $\beta$ -rays with the velocities 0.91, 0.74, 0.66, 0.60, 0.42, and 0.38. The intensities of the lines on the two photographs indicate that the rays 0.91, 0.74, 0.66, and 0.60 are due to actinium-X and the active deposit, whilst the rays 0.53, 0.49, 0.43, and 0.38 are due to radio-actinium.

The highly penetrating rays which have been previously referred to (A., 1908, ii, 1007) are now shown to be  $\gamma$ -rays. II. M. D.

**Analysis of the  $\gamma$ -Rays from Radium-B and -C.** ERNEST RUTHERFORD and H. RICHARDSON (*Phil. Mag.*, 1913, [vi], 25, 722-734).

An analysis of the  $\gamma$ -rays of radium, now known to be complex, and due in part to radium-B as well as radium-C, has been made by absorption methods. An  $\alpha$ -ray tube, filled with radium emanation, was placed in a magnetic field to deflect primary  $\beta$ -rays, and the ionisation in the electroscope measured both in air and in a mixture obtained by passing hydrogen through methyl iodide, in order to exaggerate the relative effect of the very easily absorbed radiation. After passage through 6 cm. of aluminium, the absorption is exponential with the value  $\mu=0.115$  or  $\mu/D=0.0424$ , as found by Russell and Soddy. Between 0.5 and 6 cm. of aluminium, a curve was obtained which, when the effect of the hard  $\gamma$ -rays was subtracted, was exponential with the value  $\mu=0.51$  in aluminium. This is due to radium-B. Similarly, between 0 and 0.08 cm. of aluminium, a radiation, exponentially absorbed with  $\mu=40$ , was obtained. Evidence of a still softer radiation ( $\mu=230$ ) was also obtained, but it is inconclusive.

From pure radium-C, deposited on nickel by von Lerch's method, the radiation is exponentially absorbed ( $\mu=0.115$ ) after 0.2 cm. of aluminium. A soft radiation was present, but it was probably due to a secondary characteristic radiation from nickel, and was not observed when silver was used. When lead was used as the absorbent, the soft radiations from radium-B were not exponentially absorbed, and the value of  $\mu$  varied from 11 to 2.8.

Thus, radium-B emits certainly two, and perhaps three, types of  $\gamma$ -rays, whilst radium-C emits only one. The radiation,  $\mu=40$ , corresponds with the characteristic X-radiation in the L series to be expected from an element of atomic weight 214. The second type,  $\mu=0.51$ , probably corresponds with another series not so far observed for the X-rays. The energy of the softer type of  $\gamma$ -rays from radium-B ( $\mu=40$ ) is very small compared with that of the more penetrating types from radium-B and -C. F. S.

**Production of Photochemically Active Rays in Ordinary Chemical Reactions.** J. HOWARD MATHLWS and LEON H. DEWEY (*J. Physical Chem.*, 1913, 17, 230-234. Compare A., 1912, ii, 116).

—When zinc is dissolved in acid, or calcium carbide is acted on

by water in proximity to a photographic plate, and the gases evolved are led away, the plate remains unaffected. When, however, as in Matuschek and Nenning's experiments (A., 1912, ii, 116), the gaseous products are allowed to come into contact with the plate, reduction occurs, and images are formed of pieces of tin, etc., laid upon the plate in such a way as to protect it from the gases. Writing may be produced on a photographic plate, using a jet of hydrogen as a pen and afterwards developing.

No photographic effect could be detected in the case of reactions, such as the slaking of lime, which give no gaseous products. The conclusion is drawn that Matuschek and Nenning's chemically active rays do not exist. R. J. C.

**The Rontgen Ray Luminescence of Mercury Vapour.** S. LANDAU and H. PIWISKIEWICZ (*Physikal. Zeitsch.*, 1913, 14, 381-386). - It is shown that the action of X-rays on mercury vapour causes the emission of a bluish green light. The intensity of the luminous emission increases with rise of temperature, but this is entirely due to the increase in the density of the saturated vapour. For observations with unsaturated mercury vapour, it appears that the temperature of itself has no influence on the intensity of the luminosity.

The luminosity becomes less intense when foreign gases are admixed with the mercury vapour. The comparative observations made with nitrogen, carbon dioxide, and hydrogen show that the first two gases have approximately the same influence, while hydrogen is appreciably more active in reducing the luminosity. The spectrum of the X-ray luminescence appears to be continuous with a maximum intensity at about  $\lambda = 410\mu$ . H. M. D.

**Relationship between the Fluorescent Rontgen Rays.** W. KAUFMANN (*Physikal. Zeitsch.*, 1913, 14, 386-387). - It has been pointed out by Owen (A., 1912, ii, 516) that the absorption by various gases of the characteristic fluorescent rays which are emitted by the elements between iron and molybdenum is proportional to the fifth power of the atomic weight of the radiator. This relationship would appear to hold whatever the nature of the absorbing substance, and, furthermore, to be applicable to fluorescent rays of either the *L* or the *K* group. If the logarithms of the atomic weights of the radiators are taken as abscissae, and the logarithms of the specific absorption of the characteristic rays in aluminium as ordinates, points are obtained which lie on a straight line, the tangent of the slope of which is very nearly equal to 5. For the two groups of rays, the lines are practically parallel. The *L* rays emitted by a metal have the same properties as the *K* rays emitted by another metal, the atomic weight of which is 1.27 of that of the first metal. H. M. D.

**Demonstration of Fluorescent Rontgen Radiation.** W. KAUFMANN (*Physikal. Zeitsch.*, 1913, 14, 387-388). - An apparatus has been designed which affords a convenient means of demon-

strating the emission of fluorescent secondary rays by different metals when these are subjected to the action of Röntgen rays. In this apparatus, arrangements are made for moving disks of various metals into such a position that they are exposed to the rays from the anti-cathode of an X-ray bulb, which is placed so that the rays pass through an aperture in a lead plate into a wooden box, which on its lower side is provided with a narrow observation tube. Attached to the lower side of the lead plate which covers the top of the wooden box is a fluorescent screen, which is so arranged that it can only be acted on by the secondary rays emitted by the metal in front of the aperture, and not by the primary rays. By the movement of a rod to which the metal disks are attached, these can be brought into position at will and examined in respect of their behaviour towards the primary rays. By varying the pressure in the discharge tube, the character of the primary rays is readily varied, and the different metals can be compared at various stages of exhaustion. H. M. D.

**Carriers of the Negative Thermionic Current in a Vacuum.** GWILYM OWEN and ROBERT HALLSALL (*Phil. Mag.*, 1913, [vi], 25, 735-739).—The authors have made further experiments to determine the nature of the ions which are emitted at high temperatures by palladium, pure and commercial platinum, and iridium. From the influence which a magnetic field exerts on the negative thermionic current, it appears that the carriers consist almost entirely of electrons, and that if heavy ions are present at all, the proportion of the current carried by them is less than one two-thousandth, and probably less than one ten-thousandth, even at the highest temperatures. H. M. D.

**The Actinium Products of Long Life.** OTTO HAHN and MARTIN ROTHENBACH (*Physikal. Zeitsch.*, 1913, 14, 409-410).—Actinium, radioactinium, and actinium-X have been obtained in as pure state, in the radioactive sense, as possible in order to determine the periods of the changes, and whether actinium itself gives a detectable radiation.

Actinium-X was prepared from radium-free actinium by precipitating the actinium and radioactinium with ammonia, adding iron to the acidified filtrate, and again precipitating with ammonia, and removing the actinium-X from the filtrate by a barium sulphate precipitation. The half-period, determined as the mean of a large number of closely agreeing decay curves of the  $\beta$  rays, was 11.6 ( $\pm 0.1$ ) days ( $1 \lambda(\text{day})^{-1} = 16.8$ ). The usually accepted values are 10.2 and 15 days respectively.

Radioactinium was prepared by precipitating zirconium in a feebly acid solution of actinium by sodium thiosulphate and purifying the precipitate from actinium by repetition of the process. The  $\beta$ -ray decay curve agreed with the theoretical, for the half-periods of 19.5 days and 11.6 days for radioactinium and actinium-X respectively, and was exponential from the 115th to the 174th day from preparation, when the  $\beta$ -rays became too small for measure-

ment. After 450 days no  $\alpha$ -radiation could be detected, showing that there is no appreciable residual activity. The value of  $1/\lambda(\text{day})^{-1}$  for radioactinium is thus 28.2, in agreement with previous values.

Actinium was purified repeatedly from its products, as rapidly as possible to minimise their regeneration, and initially gave no detectable  $\beta$ -rays and only a very small trace (0.2 to 0.3% of the maximum) of  $\alpha$ -rays. The possibility is not excluded that actinium may give a very strongly absorbed  $\beta$ -radiation, which, like that of radium-D, could be shown only by photographing the magnetic spectrum of the  $\beta$  rays.

F. S.

**The Existence of Uranium-Y.** ALEXANDER FLECK (*Phil. Mag.*, 1913, [vi], 25, 710—712).—All attempts to repeat the work of Antonoff (A., 1911, ii, 814), who obtained evidence of a product, uranium-Y, with period 1.5 days, giving soft  $\beta$ -rays and some  $\alpha$  rays, and present in the uranium series in minute quantity, have been unsuccessful. Various methods of removing thorium in minute amount from large amounts of uranium proved incomplete, and with such uranium, the presence of thorium-B gave effects similar to those observed by Antonoff. With uranium, free from thorium, no trace of any other product except uranium-X was obtained.

F. S.

**Growth of Radiothorium from Mesothorium 2.** JOHN A. CRANSTON (*Phil. Mag.*, 1913, [vi], 25, 712—715).—The object was to ascertain whether the production of radiothorium from mesothorium-2 was direct or occurred through an intermediate product, the parent of ionium, the analogue of radiothorium in the uranium series, being experimentally still unknown. By adding a trace of thorium to the mesothorium-barium solution, and precipitating with ammonia, mesothorium-2, radiothorium, and thorium-B and C are obtained with the thorium. The precipitate, dissolved in the smallest quantity of acid, is treated with hydrogen peroxide, and the thorium and radiothorium removed, the final traces of thorium-B and C being removed by adding a lead and bismuth solution and precipitating with hydrogen sulphide several times. The pure mesothorium-2 preparation was examined in a magnetic field to deflect  $\beta$ -rays from the electroscopes, and the growth of  $\alpha$  rays with time observed. The curves agreed with the theoretical curves, calculated on the assumption that the production of radiothorium occurs directly, except over the initial few hours, when a rapid decay of an initial  $\alpha$  radiation rather than a rise from zero occurred. The difference curve is approximately exponential with the period of mesothorium 2, and suggests the possibility that some of the mesothorium-2 atoms disintegrate, with expulsion of an  $\alpha$  ray instead of a  $\beta$  ray. The proportion, however, cannot be greater than 3 in 100,000, and owing to the similarity of period between mesothorium-2 and thorium-B, the point is left open for further examination.

F. S.

**The Preparation of Radioactive Substances from Thorium.** FRITZ GLASER (*Chem. Zeit.*, 1913, 37, 477-478).—A substance, with activity corresponding with that of thorium-X, has been separated by means of the insolubility of its sulphate from the sulphuric acid solution of monazite sand. This substance, which is termed provisionally thorium-Y, as its manner of preparation is different from that of thorium-X, is left undissolved when thorium phosphate, precipitated by neutralising or diluting the monazite solution, is treated with sulphuric acid. F. S.

**Radioactivity of Typical Soils in the United States.** RICHARD B. MOORE (*Biol. Zentr.*, 1913, 42, 213; *Internat. Cong. Appl. Chem.*, 1912).—The radioactivity of twelve soils was investigated by Strutt's method. The radioactivity seems to be connected with the mineral composition rather than with the chemical composition. No definite conclusions could, however, be drawn. N. H. J. M.

**Anomalous Dispersion in the Region of Short Electric Waves.** F. ECKERT (*Ber. Deut. Physikal. Ges.*, 1913, 15, 307-329).—Experiments have been made to determine the behaviour of metals, water, and alcohols towards electric waves of short wavelength. The wave-lengths examined ranged from 17.5 to 88 mm. In contrast with certain previous statements, it has been found that the reflexion capacity of the metals amounts to 100% in agreement with theoretical requirements. This result is independent of the position of the plane of the electric vector.

Absorption measurements were made for water, methyl, ethyl, propyl, and isobutyl alcohols, and for glycerol, and in all cases anomalous dispersion was found in the region of wave-lengths submitted to examination. It is suggested that the absorption of these substances is not due to the presence of the hydroxyl group, but to the complex molecules which are formed as a consequence of association. The variation of the absorption with temperature is in agreement with this view. H. M. D.

**Influence of the Valency of the Metal on the Photo-electrical Effect of Metallic Compounds.** G. A. DIMA (*Compt. rend.*, 1913, 156, 1366-1368).—The author has compared the photo-electrical effects produced by salts of metals, capable of yielding two or more classes of compounds with varying valency of the metal, such as mercury, tin, iron, copper, etc., and in all cases finds that the compound in which the valency of the metal is least appears to have the greatest photo-electrical power. W. G.

**Cathodic Sputtering.** GEORGE W. C. KAYE (*Proc. Physical Soc. London*, 1913, 25, 198-201).—An account is given of the volatilisation of an aluminium cathode in a discharge tube containing helium. The cylindrical electrodes were made by bending thin sheets of aluminium so that two opposite edges were nearly in contact. The sputtered deposit which appeared on the glass walls when the discharge was run at a moderate potential indicates that the



disintegration of the aluminium was practically restricted to the edges of the cathode. This would seem to show that the particles are shot off exclusively from those regions where the potential gradient has a maximum value. H. M. D.

**Calculation of Equivalent Conductivity at Infinite Dilution.** STUART J. BATES (*J. Amer. Chem. Soc.*, 1913, **35**, 519-535).—In interpreting the results of an investigation of the properties of solutions of electrolytes, the concentrations both of the ions and of the non-dissociated molecules must be known with considerable accuracy, and this involves an exact knowledge of  $\Lambda_0$ . The methods employed by Kohlrausch and Noyes for calculating  $\Lambda_0$  values are discussed, and it is shown that these demand the assumption that the expression  $(\gamma)^2/C(1-\gamma)$  for the ionisation constant becomes zero at zero concentration. Graphic and algebraic methods for determining the value of  $n$  in Storch's equation (A., 1896, ii, 288) are developed. The variations of  $n$  with the concentration are compared for weak, medium, and strong electrolytes, and it is shown that, in all cases, as the concentration decreases, the value approaches more closely to that required by the law of mass action.

Methods are given for calculating the upper and lower limits between which the value of  $\Lambda_0$  must lie. In the case of the uni-univalent salts for which Kohlrausch obtained data for solutions as dilute as 0.0001N, the difference between the limits is about 0.2%. An empirical graphic method is described for determining an upper limit and a "probable" value of  $\Lambda_0$ . The limiting values and "probable" values have been calculated for several salts, and show good agreement. The "probable" values have been adjusted by Kohlrausch's law of the independent migration of ions, and the resulting  $\Lambda_0$  values are smaller than those generally employed. E. G.

**Conductivity Maxima in Glycerol.** STEWART J. LLOYD (*J. Physical Chem.*, 1913, **17**, 264-267).—Zinc chloride appears to be indefinitely soluble in glycerol at 150°. The solutions exhibit a maximum conductivity at 50° with 0.188 gram of zinc chloride per c.c., and at 100° with 0.271 gram. The maximum had not been attained at 150° with the strongest solution measured, namely, 0.6131 gram per c.c.

The falling off in the conductivity in concentrated solutions is held to be closely connected with the increased viscosity. The temperature-coefficient is very large, corresponding with a rapid fall in viscosity as the temperature is raised. Concentrated solutions solidify to a jelly-like paste on cooling from 150°. R. J. C.

**Electric Conductivity of Mixtures of Selenious Acid and Ammonia.** EUGÈNE CORNÉC (*Ann. Chim. Phys.*, 1913, [vi], **28**, 697-701).—Measurements have been made of the electric conductivity of solutions obtained by mixing aqueous solutions of ammonia and selenious acid in different proportions. Five series of experiments were made, in which the concentrations of the

alkaline and acid solutions were respectively 1.8, 1.16, 1.32, 1.61, and 1/128 molar. The results are shown by a series of curves obtained by plotting the molecular conductivity as a function of the ratio of the proportions of the constituent solutions. The conductivity curves for the three most dilute solutions exhibit a minimum at the point corresponding with the acid selenite,  $\text{NH}_4\text{HSeO}_3$ , and in all cases the curves show a maximum at the point corresponding with  $(\text{NH}_4)_2\text{SeO}_3$ . There is no evidence of the formation of any other compound, as was suggested by the results obtained by Miolati and Mascetti (A., 1901, ii, 381). H. M. D.

**Citrophosphate Solutions. III. The System Citric Acid-Phosphoric Acid-Sodium Hydroxide-Water.** UGO PRATOLONGO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 387—391. Compare this vol., ii, 282).—The author has investigated at 29° that part of the diagram of this system in which the production of citrophosphate compounds is most probable, and from the results (which are exhibited in curves) no evidence of the existence of citrophosphate can be obtained. The only solid phases observed were citric acid, monosodium citrate and disodium phosphate. R. V. S.

**Aqua Regia. II. Effect of Chloride Ion on the Potential of the Nitric Acid Electrode.** WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1913, 35, 333—340).—In an earlier paper (A., 1911, ii, 719) it has been shown that the chloride ion decreases the efficiency of dilute nitric acid in the oxidation of ferrous salts. In order to find an explanation, a study has been made of the effect of chloride ions on the oxidation potential of nitric acid. An attempt was made to obtain a value for the oxidation potential of a  $N/10$ -nitric acid electrode, saturated with nitric oxide, but constant results could not be obtained on account of the increase in the concentration of nitrous acid due to the reduction of the nitric acid by the nitric oxide and by the reduction of nitrate to nitrite ions. The experiments showed, however, that the potential of the nitric acid electrode was reduced in presence of the chloride ion, this being due probably to a decrease in the tendency towards nitrite ion formation.

The oxidation potential of  $N/10$ -nitric acid in equilibrium with nitrous acid and nitric oxide at atmospheric pressure is quite definite, and the chloride ion has no effect on it. The mean value of this potential is 0.4723 volt, measured against a  $N/10$ -calomel electrode at  $25.17 \pm 0.02^\circ$ . E. G.

**Potential of the Lithium Electrode.** GILBERT N. LEWIS and FREDERICK G. KEYES (*J. Amer. Chem. Soc.*, 1913, 35, 340—344).—The potential of the lithium electrode has been determined by a modification of the method employed in the case of the sodium and potassium electrodes (A., 1910, ii, 1027; 1912, ii, 225). The results show that the potential of lithium in a  $N$ -solution of lithium ions at 25° is 3.3041 volts against the normal calomel electrode taken as zero. This value is the sum of (1) 2.3542 volts, the potential of lithium amalgam (containing 0.0350% Li) against an aqueous

solution containing lithium ions in  $N$ -concentration, and (2) 0.3592 volt, the difference of potential between lithium and 0.0350% lithium amalgam in a solution of lithium iodide in propylamine.

The temperature-coefficient of the latter  $E.M.F.$  is 0.000323 volt per degree, and hence the heat of solution of 1 gram-atom of lithium in 0.0350% lithium amalgam is -19,605 cal. E. G.

**An Apparatus and a Method for the Determination of the Velocity of the Chemical Reactions which take place on Electrodes during the Passage of a Current.** DAVID REICHSTEIN (*Zeitsch. Elektrochem.*, 1913, 19, 384-389).—The apparatus used in the investigation consists of a multiple rotating commutator, by means of which the primary and secondary currents can be made and broken at definitely known intervals of time. The author deduces expressions which give the velocity constants for reactions of the first and second order. They have the forms:  $k_0 = (m_0 - m)/mt$  and  $k_0^2 V = (m_0 - m)^2/m_0^2 t m^2$  respectively, where  $k_0$  is the constant of the velocity of decomposition (for example, in the decomposition of the platinum hydrogen alloy with the formation of molecular hydrogen),  $m_0$  is proportional to the quantity of copper deposited in a copper coulombmeter in the secondary circuit,  $m$  to a similar value in the primary circuit,  $t$  represents the time from the commencement of the experiment at which the values  $m_0$  and  $m$  were obtained, and  $V$  is the volume occupied by the reacting substance on the electrode. The method is used for determining the velocity of evolution of oxygen from a platinum electrode. The results are regarded as orienting only. J. F. S.

**Electromotive Force Produced by the Flow of Solutions of Electrolytes through Capillary Tubes.** LOUIS RIÉRY (*Compt. rend.*, 1913, 156, 1368-1370).—An extension of the measurements of the  $E.M.F.$  produced by the flow of electrolytic solutions through capillary tubes (compare A., 1912, ii, 622) to solutions of potassium chloride, nitrate, sulphate, and hydroxide, and hydrochloric and sulphuric acids of varying concentrations. By determining the viscosity and conductivity of the solutions, the author has also calculated the potential difference at the point of contact of the glass and the electrolyte. The values of this potential difference in the case of potassium nitrate steadily decrease as the concentration increases, showing no minimum up to a concentration of 1 gram-molecule per litre. For dilute solutions, the potential difference at the point of contact is much less for potassium salts than for copper salts (*loc. cit.*). W. G.

**New Processes for the Production of Electricity which Explain Some Bioelectrical Phenomena.** REINHARD BAUTSE (*Zeitsch. Elektrochem.*, 1913, 19, 319-330).—The various theories which have been propounded to explain the origin of the potential difference occurring at membranes are discussed (compare Oswald, A., 1909, ii, 1351; Walden, A., 1903, ii, 203). Experiments are described which imitate the processes on living membranes. Leeb

(A., 1912, ii, 663) has shown that the biological potential differences are reversible for cations of different kinds, and the author shows that this can be imitated by means of substances which are insoluble in water, but which possess acidic properties, for example, salicylaldehyde saturated with salicylic acid. The physical character of the phenomenon can be explained by the Nernst hypothesis for the potential difference between two immiscible phases, and from the experimental data furnished by such mixtures, for example, the potential difference of dimethylaniline and salicylaldehyde mixtures, which show reversibility for ions of similar charge. In this particular case the explanation is as follows: It is assumed that in the regions, on both sides of the dividing layer, a double decomposition occurs between the various electrolytes, and from differences of solubility of the two changed products in the different layers, a diffusion occurs which causes an increase in the concentration of the ions, and it is in respect of these that the reversibility occurs. From the Nernst theory the division layer behaves as an electrode. In accordance with the foregoing a formula is deduced for the salicylaldehyde potential differences which agrees well with the experimental data.

J. F. S.

**A New Kind of Electromotive Force and Some Possible Applications to Physico-chemical Problems.** REINHARD BREITNER (*J. Amer. Chem. Soc.*, 1913, 35, 341—352).—An account is given of certain galvanic cells composed of insoluble organic liquids and aqueous solutions, such as:

— $N/10\text{ KCl} \mid \text{salicylaldehyde} \mid N/1250\text{ KCl} +$ , which has an *E.M.F.* 0.083 volt. The potassium chloride can be replaced by almost any other soluble salt. These phenomena can be explained by assuming that the  $K^+$  concentration of the salicylaldehyde is due to the presence of salicylic acid, which reacts with the potassium chloride with formation of potassium salicylate and hydrochloric acid. It is probable that owing to a difference in the solubility of these products in salicylaldehyde they are not equally distributed between the two phases (salicylaldehyde and water), and the effect of this unequal distribution is that the concentrations of  $K^+$  in water and in salicylaldehyde are not proportional. A theory has been evolved according to which the change of the potential difference with the concentration must become more like that at a metal electrode the smaller the concentration. These considerations have shown that, besides salicylaldehyde, other insoluble organic substances show a similar change in the potential difference with the concentration of the aqueous solution provided that (1) the substance contains a strong acid, capable of reacting with the salt of the aqueous solution; and (2) the concentration of the salt produced by the reaction in the insoluble organic substance is far greater than the potassium chloride concentration. In the case of benzaldehyde, the effect of the concentration on the potential difference is less marked, since benzoic acid is a weaker acid than salicylic. If benzyl alcohol is used, no *E.M.F.* is observed, and with phenol only a very small *E.M.F.* is found.

If, in place of the salicylaldehyde, aniline or toluidine is employed, a change of potential is observed in the opposite direction. As water is slightly soluble in aniline, the compound  $\text{Ph}\cdot\text{NH}_2\cdot\text{OH}$  may be supposed to be formed, which would react with potassium chloride, thus:  $\text{Ph}\cdot\text{NH}_2\cdot\text{OH} + \text{KCl} = \text{Ph}\cdot\text{NH}_2\cdot\text{Cl} + \text{KOH}$ , the aniline behaving like a reversible  $\text{Cl}^-$  electrode. In the case of the cell  $+N/10\text{-KCl} \mid \text{toluidine} \mid N/1000\text{-KCl}-$ , an *E.M.F.*  $-0.105$  volt was observed, and similar *E.M.F.*'s were found with xylydine and methylaniline.

All these cells are mere concentration cells, the *E.M.F.* being due to the difference in concentration of two solutions of the same salt. In the case of cells composed of solutions of two different salts of equivalent concentration, the *E.M.F.*'s produced are nearly as large as those of cells with metal electrodes.

Several applications of these phenomena are discussed. E. G.

**New Electric Properties of a Semipermeable Membrane of Copper Ferrocyanide.** REINHARD BETXER (*J. Physical Chem.*, 1913, 17, 344—360. Compare Loeb and Beutner, A., 1912, ii, 663).—A precipitation membrane of copper ferrocyanide behaves as an electrode, reversible for various univalent positive ions, but, unlike the vegetable membranes previously investigated, indifferent to bivalent cations.

The experiments described were made with an open tube of gelatin jelly, containing potassium ferrocyanide, bathed at one end in copper sulphate solution, so that a membrane was formed at the surface of the jelly. On connecting the copper sulphate solution and the top of the jelly to calomel electrodes by potassium chloride solution, the potential was from 0.10 to 0.13 volt, whereas the liquid potentials in the circuit could hardly exceed 0.01 volt. The contact *E.M.F.* of the ferrocyanide membrane appears to be due to the difference in potassium concentration on either side of it. On the one side is the potassium ferrocyanide, and on the other, in the copper sulphate solution, is the potassium sulphate generated by the formation and steady increase in thickness of the membrane. When the diffusion away of potassium sulphate is accelerated by stirring the copper sulphate solution, the *E.M.F.* rises temporarily.

Univalent positive ions must be able to diffuse into the membrane, which, it is suggested, consists of a complex compound of copper and potassium ferrocyanides. The *E.M.F.* observed is opposite in sign to that given by metallic electrodes in concentration cells, since these are only sensitive to anions.

The effects of varying the composition and concentration of the electrolytes bathing a ferrocyanide membrane are in accordance with the author's views. R. J. C.

**Constitution of Certain Liquid Amalgams.** JOEL H. HULME BRAND (*J. Amer. Chem. Soc.*, 1913, 35, 501—519).—The formula given by the author for the *E.M.F.* of liquid amalgam concentration cells (*Trans. Amer. Electrochem. Soc.*, 1913, 22, 319) has now been integrated exactly by the aid of the vapour pressure law, and

applied to the amalgams of zinc, lead, tin, thallium, indium, and cadmium.

In the case of zinc amalgams, the results of *E.M.F.* and vapour pressure determinations are in good agreement, and indicate that the zinc is not combined with the mercury, but is associated in accordance with the equation  $2\text{Zn} = \text{Zn}_2 + 2100$  joules. The equilibrium constant of this reaction and the degree of dissociation at different dilutions are given and are shown to accord well with the measurements of *E.M.F.* and its temperature-coefficient. The same formula applies to the lead and tin amalgams, but with a different constant, corresponding with a much greater degree of association. The thallium amalgams give results corresponding with the formula for cases in which combination occurs. Indications have been obtained of the compound  $\text{TlHg}_2$ , which in the more concentrated amalgams seems to break up into a simpler compound, probably  $\text{TlHg}$ . Indium amalgams appear to contain  $\text{InHg}_2$ , which is converted into a simpler compound in the more concentrated amalgams. Cadmium amalgams seem to contain both free cadmium and the compound  $\text{CdHg}$ , in proportions depending on the law of mass action; in the most dilute amalgams, two-thirds of the cadmium is present in the combined state.

The validity of the fundamental formula is discussed, and it is shown to be of considerable value for determining the constitution of metallic solutions and for investigating the unknown factors which influence the vapour pressure of solutions. E. G.

**The Spontaneous Charging of Photo-electric Cells in the Dark and the Nature of the Active Rays of Potassium.** HANS THUNING (*Physikal. Zeitsch.*, 1913, **14**, 406–408).—Experiments are described which show that the acquisition of a negative charge by the potassium of a photo-electric cell when this is kept in the dark is not due to the emission of positively charged particles, but is simply a Volta effect. The potassium cell behaves like a galvanic element with an *E.M.F.* of about 2.8 volts, and with an internal resistance of the order of  $10^6$  ohms. The magnitude of this resistance affords a measure of the ionisation which results from the potassium radiation. H. M. D.

**A Special Type of Polarisation in Connexion with Self-induction in Concentration Cells.** JOHANNES J. VAN LAAR (*Chem. Weekblad*, 1913, **10**, 305–313. Compare van Deventer, this vol., ii, 11).—A theoretical paper, in which the author discusses the cause of a special type of polarisation only observed with zinc and allied metals. The name "polarisation due to impotence" is proposed for the phenomenon. A. J. W.

**Polarisation Through Impotence.** CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1913, **10**, 369–370. Compare preceding abstract).—A criticism of van Laar's paper, and a suggestion of the title, "Potential anomaly through impotence," as better describing the phenomenon than that given by van Laar. A. J. W.

**Hydrolysis of Salts of Strong Acids.** JOHANNES J. VAN LIAAR (*Chem. Weekblad*, 1913, 10, 334—345).—A theoretical paper investigating the influence of possible hydrolysis in very dilute salt solutions on the *E.M.F.* of a concentration cell. The author considers that even for great dilution with salts of strong acids the influence of hydrolysis is a negligible factor. A. J. W.

**Electrolysis of Crystalline Compounds. I. Silver Iodide.** GIUSEPPE BRUNI and G. SCARPA (*Atti R. Acad. Lincei*, 1913, [v], 22, i, 433—443).—The authors immersed two silver electrodes in fused silver iodide, and after solidification passed a current between them. The anode dissolved, and silver was deposited on the cathode. The deposited silver tended to form threads pointing towards the anode, and unless weak currents (0.1 ampere) were passed, it was difficult to avoid their becoming connected. In quantitative experiments at 160°, 200°, 250°, 300°, and 400°, Faraday's laws were verified. If silver iodide possesses a metallic as well as an electrolytic conductivity (as has been suggested), it must constitute only a very minute fraction of the total conductivity. R. V. S.

**The Electrolytic Regeneration of Chromic Acid from Solutions of Chromium Sulphate.** PAUL ASKENASY and A. RIVAI (*Zeitsch. Elektrochem.*, 1913, 19, 311—362).—The paper deals with the regeneration of chromic acid from chromium sulphate by anodic oxidation in cells without diaphragms. The oxidation occurs readily on lead anodes with excellent current efficiency; the object of the investigation is to define the cathode conditions, so that only a minimum of reduction shall occur there, and so make it possible to work without a diaphragm. The experiments were made with a solution containing 81 grams of chromic acid in 500 c.c. of solution and so much sulphuric acid as corresponds with an excess of 19%, when all the chromic acid has been converted into chromic sulphate. This corresponds to the solution which is technically employed for the regeneration of chromic acid. It is shown that at the commencement of the regeneration, that is, when the concentration of chromic acid is small, it is better to use low current densities at the cathode, and to increase the current density as the concentration of chromic acid increases. Temperature has little influence on the process. The addition of magnesium sulphate prevents reduction at the cathode when dilute solutions and low current densities are employed, but if there is only a small percentage of chromic acid present it has the opposite effect, and if high current densities are used it has no effect. The influence of chromium sulphate is to prevent reduction with both high and low current densities except in solutions which contain very little chromic acid. The addition of sodium and potassium sulphates is without influence on the reaction. Dilution is favourable to the oxidation under all circumstances, but more especially with high current densities and in the presence of magnesium sulphate when low current densities are employed. A high concentration of sulphuric acid has a slightly favourable action. The following conditions are found to be most successful for the technical regeneration of chromic acid. The con-

centration of chromic acid must not exceed 100 grams per litre, the cathode current density should be above 200 amperes per sq. decimetre, under which conditions the addition of other salts becomes unnecessary. Should other conditions be chosen, the addition of other salts must be made cautiously, as, although they allow a high concentration of chromic acid to be obtained with good current efficiency, the current efficiency is very poor when only a small concentration of chromic acid is present. A complete list of the literature on the electrolytic deposition of chromium metal is appended to the paper.

J. F. S.

**Coefficient of Magnetisation of Water and Oxygen.** AUGUSTE PICCARD (*Arch. Sci. phys. nat.*, 1913, [iv], 35, 201-231).—Details are given of the methods adopted for the determination of the strength of the field employed in the magnetisation experiments which were made according to Quincke's meniscus method. No results are communicated in the present paper.

H. M. D.

**Magnetic Induction in Ferric Oxide at Various Temperatures and in Different States and the Possible Chemical Changes Indicated by the Observations.** GEORGE E. ALLAN and JOHN BROWN (*Proc. Roy. Soc. Edin.*, 1913, 33, 69-84).—The magnetic properties of artificial and natural ferric oxide have been examined with special reference to the influence of temperature. It was found that both pure artificial ferric oxide and impure hematite become magnetic when heated in air in a magnetic field. On cooling from about 1000° both substances were found to have become more or less permanently magnetised. The effect is attributed to the formation of ferroso-ferric oxide.

When the pure oxide was heated in hydrogen, the temperature at which the substance acquired magnetic properties was higher (300°), but this temperature was much more sharply defined than when the oxide was heated in air. The curves which show the dependence of the magnetic effect on the temperature in the case of the oxide heated in hydrogen have maxima at 425°, 575°, and 750°, and these are supposed to indicate the optimum temperatures for the various stages in the reduction of the ferric oxide.

H. M. D.

**Magnetic Researches. VII. Paramagnetism at Low Temperatures.** H. KAMERLINGH ONNES and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913 15, 965-971. Compare A., 1912, ii, 228, 425, 1133).—The variation of the magnetic susceptibility of crystallised manganous sulphate ( $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ) with temperature is found to be in accordance with Curie's law between 0° and about -200°. At liquid hydrogen temperatures deviations occur. The anhydrous salt behaves differently, in that the value of  $\chi(P-\Delta)$  remains constant down to -210° if  $\Delta=21$ . As in the case of ferrous sulphate, the presence of water of crystallisation causes  $\Delta$  to become equal to zero. For both manganous and ferrous sulphates, the number of magnetons in the crystalline and anhydrous salts



is the same, and in both cases the number is one less than that which appears to be characteristic of the dissolved salt.

Some observations have also been made on the susceptibility of platinum and liquid oxygen. In the case of platinum the susceptibility changes very little between the ordinary temperature and  $-260^{\circ}$ . Between  $64.9^{\circ}$  abs. and  $90.1^{\circ}$  abs. the relationship between the susceptibility of liquid oxygen and the absolute temperature can be expressed by  $\chi(T+71) = \text{constant}$ . Since gaseous oxygen obeys Curie's law at temperatures above that of the room, it would appear that there is a change in its behaviour at some point between  $-180^{\circ}$  and  $0^{\circ}$ .  
H. M. D.

**Thermometry.** JOHN H. COSTE (*J. Soc. Chem. Ind.*, 1913, 32, 341—345).—A discussion of the errors affecting the mercury thermometer.  
T. S. P.

**Isotherms of Monatomic Substances and of their Binary Mixtures.** XIV. Calculation of Some Thermal Quantities for Argon. H. KAMERLINGH ONNES and C. A. THOMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 952—960. Compare A., 1912, ii. 900).—From the coefficients of the empirical equation of state for argon, the authors have calculated the values of a number of thermodynamic quantities. These are utilised for a comparison of the behaviour of argon with that of isopentane, and it is shown that in several respects there is a close similarity in the behaviour.  
H. M. D.

**Thermal Conductivity, Specific Heat, and Viscosity of Gases.** ARNOLD ECKEN (*Physikal. Zeitsch.*, 1913, 14, 324—332).—The question of the partition of energy in the collision of gas molecules is discussed with reference to the variation of the phenomenon of partition according to whether the energy is translational, rotary, or vibrational. In this connexion, a comparison is made between the values of  $K$ , given by the equation  $K = k \cdot c \cdot \eta$ , where  $k$  is the thermal conductivity,  $C$  the specific heat at constant volume, and  $\eta$  the viscosity, and the corresponding values calculated on the basis of the kinetic theory. The comparison is made for a considerable number of gases of varying degrees of molecular complexity, and it is found that in several cases the observed and calculated values are in good agreement, indicating that the energy exchange is practically complete. In other cases the observed values are smaller than the theoretical numbers. This behaviour is confined to the polyatomic gases, but is also shown by helium, especially at low temperatures.

Reference may be made to the tabulated data for the thermal conductivities, which have been measured at  $0^{\circ}$ , and in some cases at  $-252^{\circ}$ .  
H. M. D.

**Expansion of Vapours and their Specific Heats.** Application to Vapour Engines. ANTON LANGE (*Ann. Chim. Phys.*, 1913, vol. 28, 577—612).—A method of calculating the ratio of the specific heats of vapours at constant pressure and volume is described. The

formula involves a knowledge of (*a*) the compressibility of the vapour at the temperatures under consideration; (*b*) the pressure of the saturated vapour and its variation with temperature; and (*c*) the latent heat of vaporisation and the specific heat of the liquid, and the variation of these with the temperature.

From the available experimental observations, the requisite data have been deduced for water, ethyl ether, and benzene, and these are applied in the calculation of the specific heats and the specific heat ratio for the saturated vapours. For water, results are recorded for temperatures between 80° and 160°; for benzene, between 40° and 120°; and for ethyl ether, between 0° and 60°. In the case of benzene and ether, the ratio of the specific heats increases with the temperature according to a linear formula, but for water vapour, the relationship is more complex, and may be represented by the equation:  $\gamma = 1.373 + 0.004\theta - 0.0008\theta^2 - 0.0039\theta^3$ , where  $\theta = t^\circ - 100^\circ$ .

Similar calculations have been made for the unsaturated vapours, and the variation of the specific heat ratio with the pressure of the vapour has also been examined.

In the final section, the calculated numbers are considered with reference to the efficiency of steam and ether vapour engines, and also to the influence of superheating on the efficiency. H. M. D.

**Concentrated Solutions. II.** ÉMILE RAOU (*Ann. Chim. Phys.*, 1913, [viii], 29, 124—143. Compare A., 1912, ii, 1147).—The relation between the composition and freezing point of concentrated solutions has been further examined, and formulae deduced which are applicable to binary mixtures which absorb or evolve heat when the components are mixed together. To test the formulae, experiments have been made with mixtures of cyclohexane and ethylene bromide, cyclohexane and acetic acid, and benzene and carbon tetrachloride. For each of these pairs, the freezing-point curves and the heat changes which occur when the components are mixed in varying proportions have been determined, and it is found that the derived formulae are in fair agreement with the observed freezing points for the different mixtures.

From the freezing-point diagrams, it is seen that cyclohexane and ethylene bromide show a eutectic at  $-25^\circ$ , corresponding with about 85 mols. % of cyclohexane. The behaviour of cyclohexane and acetic acid is similar, a eutectic being obtained at  $-25^\circ$  and about 95 mols. % of cyclohexane. The cyclohexane curve is in this case characterised by a very strongly marked inflexion. The diagram for benzene and carbon tetrachloride shows that the curves for the pure substances are intercepted by a curve corresponding with the compound  $C_6H_6.CCl_4$ , which melts at about  $-34^\circ$ .

H. M. D.

**Latent Heat of Evaporation of Aqueous Salt Solutions.**  
ROBERT G. LUNNON (*Proc. Physical Soc. London*, 1913, 25, 180—191).  
—The heat absorbed in the vaporisation of steam has been measured

for a number of saturated aqueous solutions of salts, and also for a number of unsaturated solutions of varying concentration. A measured quantity of heat was supplied to the boiling solution contained in a calorimeter by means of a small electric lamp. The calorimeter was placed inside a double-walled vessel surrounded by a solution boiling at the same temperature as the solution under examination. The steam from the inner vessel escaped through a tube into a detachable condenser, the weight of which could be determined at suitable intervals.

The latent heats thus obtained for various saturated solutions were as follows, the numbers in brackets representing the respective boiling points of the solutions: Sodium nitrate ( $121.0^{\circ}$ ), 459; potassium nitrate ( $116.8^{\circ}$ ), 421; sodium chloride ( $110.0^{\circ}$ ), 508; potassium chloride ( $109.0^{\circ}$ ), 493; potassium chromate ( $106.8^{\circ}$ ), 505; potassium dichromate ( $104.8^{\circ}$ ), 489. The differences between these numbers and the corresponding latent heat values for pure water represent the heats of solution of the various salts. For the sodium and potassium salts of the same acid it appears that the heat of solution is proportional to the concentration of the saturated solution when this is expressed as grams of salt per gram of water.

From the experiments with unsaturated solutions of sodium nitrate and potassium nitrate, it is found that the latent heat is approximately constant for all concentrations until saturation is attained.

H. M. D.

**The Vapour Pressures of Liquid Tin Amalgams of Low Mercury Content.** ADOLF SIEVERTS and HERMANN OEHNE (*Ber.*, 1913, **46**, 1238—1246).—In previous investigations (compare A., 1910, ii, 851) Sieverts and his co-workers have found that diatomic gases dissolve in solid and liquid metals in a quantity which is directly proportional to the square root of the gas pressure, which behaviour can be explained on the assumption that each gas molecule, when dissolved, dissociates into the two atoms. For monatomic gases such a behaviour is improbable; the amount dissolved should be directly proportional to the pressure and in accordance with Henry's law. Attempts to show that this is the case were unsuccessful in the case of helium and argon (A., 1912, ii, 1052), owing to their insolubility, consequently the authors have determined the solubility of mercury vapour, which is known to be monatomic, in liquid tin. The method consisted in the determination of the vapour pressure of dilute amalgams, a special apparatus being designed for the purpose, in which the vapour pressure of the amalgam was balanced against the hydrostatic pressure of a column of molten tin.

The amalgams used contained 0.8–8% of mercury, and the vapour pressures for temperatures between  $300^{\circ}$  and  $360^{\circ}$  varied between 2 and 70 mm. of mercury. For this range the vapour pressure was found to be approximately proportional to the concentration, in accordance with Henry's law. The same was found to hold between the temperatures of  $515^{\circ}$  and  $528^{\circ}$  for 2 and 10% amalgams, the pressures varying from 173 to 886 mm. of mercury. T. S. P.

**Thermal Investigations in a Vacuum.** W. HEIKE (*Intern. Zeitsch. Metallgraphis*, 1913, 4, 143—151).—A new form of porcelain vessel is described for melting metals, sulphides, or arsenides out of contact with air. The vessel consists of a narrow cylinder with elongated neck. The closed end is so shaped as to form a tube, projecting into the interior of the vessel, and serving as a protecting sheath for the thermo-couple. After filling with metal, the vessel is exhausted and sealed by heating the slightly constricted neck in an oxygen blowpipe and twisting while soft. The porcelain tube is heated in a vertical electric tube furnace. Good cooling curves are readily obtained, even with sulphides and other mixtures which undergo more or less decomposition when melted in an open vessel.  
C. H. D.

**Simple Inexpensive Calorimeter for Determining the Heat of Solution and of Neutralisation.** ERNEST ANDERSON and H. A. NOYES (*J. Physical Chem.*, 1913, 17, 249—251).—The apparatus consists of a wide-mouthed Dewar bulb of about 450 c.c. capacity, closed by a rubber stopper, carrying a Beckmann thermometer, and a glass tube bearing for a rotatory glass stirrer. The rise in temperature in 400 c.c. of water due to the stirring was less than 0.001° per minute, and the fall in temperature due to heat leakage 0.01° per minute for 9° difference between internal and external temperatures. The calorimeter was designed for students' use only.  
R. J. C.

**Thermodynamic Investigations on Copper Sulphate.** A. SIGGEL (*Zeitsch. Elektrochem.*, 1913, 19, 340—344).—The paper deals with the equilibrium of the dissociation of monohydrated copper sulphate,  $\text{CuSO}_4 \cdot \text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + \text{H}_2\text{O}$ . The various quantities necessary for the calculations are redetermined in the course of the work. The heat of hydration is found to be 6592 cal. (mean) at 22°, which agrees better with the Schottky (A., 1908, ii, 1016) value of 6600 than with Thomson's value 6460. The dissociation tension was also determined at temperatures from 99° to 147.4°, and the following values found: 99°, 6.0 mm.; 110.2°, 12.0 mm.; 130.9°, 38.2 mm.; 137.2°, 53.5 mm.; and 147.4°, 90.1 mm. Using these data, the affinity is calculated, and the various factors controlled by calculations based on the Nernst thermodynamic theory. Agreement is found to be good, and to confirm the Nernst theory fully.  
J. F. S.

**Thermochemical Study of Uranyl Nitrate and its Hydrates.** ROBERT DE FORCRAND (*Compt. rend.*, 1913, 156, 1207—1210).—The author has measured the heat of solution of the four hydrates of uranyl nitrate previously described (this vol. ii, 413), and from his values has calculated the boiling point of each of them. His results differ somewhat from those of Markets (A., 1912, ii, 848). The thermochemical values obtained are in accord with the phenomena of successive dehydration exhibited by the hydrates.  
W. C.

**Ignition Temperatures, Especially of Combustibles.** H. HOLM (*Zeitsch. angew. Chem.*, 1913, **26**, 273-279).—The ignition temperature determined by the author is that at which the substance takes fire spontaneously in air at ordinary pressure. The apparatus used consisted of a vertical Heraeus furnace; a porcelain apparatus used consisted of a vertical Heraeus furnace; a porcelain crucible lid was inverted over the end of the porcelain tube in the centre of the furnace, and on the lid was one junction of a thermocouple. Gases were introduced through a narrow porcelain tube opening 1-2 mm. above the crucible lid; liquids were allowed to fall drop by drop on to the lid, whilst solids, finely powdered, were dropped on to the lid from time to time in quantities sufficient to cover the point of a knife. The experiments were made at intervals of  $10^{\circ}$  rise in temperature.

The greater majority of substances investigated were liquids; for example, petroleum, paraffin oil, ether, alcohol, benzene, etc.; the gases were ammonia, coal gas, and hydrogen, and the solids, cellulose, pent, and various coals. The solids ignite at the lowest temperatures, and the gases at the highest.

The results are fully discussed, both from the practical (industrial) and theoretical point of view  
T. S. P.

**Rectilinear Diameter for Argon.** ÉMILE MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 960-965).—For temperatures between  $-175.39^{\circ}$  and  $-131.54^{\circ}$ , the relation between the mean density of the liquid and its saturated vapour is expressed by  $D = 0.20956 - 0.0026235t$ . The slope of the rectilinear diameter is greater than that for any other substance yet investigated with the exception of xenon. On the assumption that the diameter remains rectilinear up to the critical, the above equation yields  $\rho_c = 0.53078$  for the critical density. The value previously obtained for the critical density from the argon isotherms was 0.509, and it would therefore appear that the above equation does not hold in the neighbourhood of the critical point. In this region the diameter becomes convex towards the axis of temperature.

From a comparison of the reduced density curves and diameters for ethyl ether, isopentane, oxygen, xenon, argon, and helium, it appears that the equations of state for different substances deviate to an extent which appears to be related to the divergence of their critical temperatures.  
H. M. D.

**Method of Determining Vapour Densities at High Temperatures and a New Form of Quartz Manometer.** GILBERT E. GIBSON (*Proc. Roy. Soc. Edin.*, 1913, **33**, 1-8).—The highest temperature attainable in vapour density measurements in which quartz or glass manometers are used is about  $750^{\circ}$ , but it is shown that determinations may be made at much higher temperatures if the main bulk of the vapour is heated in a quartz tube to the desired temperature and the manometer is heated separately to a temperature which is less than  $750^{\circ}$ . The manometer consists of a bulb, about 1 c.c. in capacity, which is blown on the end of a

quartz tube 3 mm. in diameter and is flattened at one end so as to form a flexible quartz membrane, about 0.1 mm. in thickness. The deformation of the membrane is recorded by an optical arrangement, and by adjustment of the pressure in an outer tube, into which the manometer tube is fitted, the deformation is reduced to zero. When suitable precautions are taken, this null method of measuring pressures is found to give accurate results. From a series of pressure readings at temperatures ranging from  $437^{\circ}$  to  $912^{\circ}$ , with a weighed quantity of mercury in the apparatus, values were obtained for the vapour density of mercury varying from 99.5 to 101.2. H. M. D.

**The Density of Double Salts.** Case of the Copper Ammonium Chlorides. EDOUARD CHACVEXET and GEORGES URBAIN (*Compt. rend.*, 1913, 156, 1320—1322).—A study of the molecular volumes of copper chloride and cupric ammonium chloride, in the hydrated and anhydrous states, leads to the conclusion that the molecular volume, like the other physical properties, obeys the law of additivity, and therefore that the molecular volume of a double salt is usually equal to the sum of the molecular volumes of its constituents. The authors consider that this double chloride can exist as a compound in the anhydrous form, although its heat of formation, as calculated for this state, is practically zero. W. C.

**The Atomic Constants and the Properties of Substances.** RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1913, 17, 173—179).—It is shown by reference to the data for about twenty organic substances that the molecular volume at the critical point can be satisfactorily represented by means of the expression  $14.04\Sigma C_r$ , in which  $C_r$  denotes the apparent volume of an atom relative to that of a hydrogen atom.

It has been shown in a previous paper that the attraction constant  $C_a$  of an atom is approximately proportional to the square root of the atomic weight ( $m$ ). A comparison is now made of the values of  $C_a$  and  $C_r$ , with  $\sqrt{m}$  for eight different elements. Considerable divergences are found in both cases, hydrogen exhibiting the largest deviations.

The formula  $T = 17.69(\Sigma C_a)^2 / (\Sigma C_r)^2$  is employed in the calculation of the critical temperatures of a number of substances, and the values compared with experiment. Association of liquid molecules tends to raise the critical temperature, and to cause deviations from the calculated value. H. M. D.

**The Elastic Limit of Alloys.** A. PORTEVIN (*Compt. rend.*, 1913, 156, 1237—1240).—The author has studied the elastic limit of alloys of three types, using Fremont's method, determining the deformation in pyramidal specimens on compression. In the case of alloys formed from a single, chemically homogeneous, solid solution, the limit of elasticity, which is a vectorial quantity for a grain, becomes scalar for the mass, since the large number of grains present all the possible orientations. The same holds good for alloys formed from a single chemically heterogeneous solid solution with an

additional complication, namely, that the elastic limit is not reached at the same time in all points of the grain. In the case of a complex of two phases presenting two constituents, one constituent is deformed first alone, and it is impossible to define by any single number the elastic limit, since it extends between limits which depend both on the mechanical anisotropy of the grains and the chemical heterogeneity of the alloy.

W. G.

**The Influence of Chemical Constitution on Interfacial Tension.** WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1913, A, 88, 303—313).—By means of a method involving the determination of the weight of the drops which are delivered by capillary tubes of known diameter, the author has measured the work which is expended in the formation of unit area of interface by the molecular forces which operate between two immiscible liquids. From experiments in which a large number of liquids were examined in combination with water, it has been found that the work done by the molecular forces varies very considerably with the chemical nature of the second liquid at which the interface is formed.

For a number of saturated substances, the value of the interfacial tension was found to vary from 20.8 to 24.5. The introduction of an ethylene linking raises the value to a considerable extent, the numbers for octane and octylene being 20.8 and 36.2 respectively. For benzene the value is 32.2. The introduction of a hydroxyl group into a ring compound increases the value by about 20 units, but the increase is only about half as large in the case of a paraffin hydrocarbon. The presence of the carbonyl group has a similar influence on the value of the interfacial tension.

In general, the interfacial tension increases with the chemical reactivity of the second liquid, the greatest values being obtained in the case of acids, alcohols, and esters. This would seem to show that the chief modifying factor in all interfaces is the development of a contact difference of potential due to polarisation of the molecules.

H. M. D.

**The Tension of Composite Fluid Surfaces. II.** WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1913, A, 88, 313—333. Compare A, 1912, ii, 838).—The problem of the spreading of one fluid over the surface of another is further considered with special reference to the changes of tension which are produced by the spreading of various liquids on water. The curves which are obtained by plotting the surface tension as a function of the thickness of the spreading layer of liquid consist in certain cases of a series of straight lines, and these are interpreted in terms of the author's theory.

H. M. D.

**Law of Hydrodiffusion of Mixtures of Potassium and Sodium Chlorides and the Dependency of the Coefficient of Diffusion of these Mixtures on the Relative Initial Concentrations of the Components.** V. S. TITOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, *Phys. Part*, 61—86).—The author has investigated the applicability to the diffusion of a mixture of two electrolytes with

a common ion of Fick's law (*Ann. Phys. Chem.*, 1855, **4**, 59), analogous to Ohm's law and to Fourier's law of thermal conductivity.

The diffusion of aqueous mixtures of potassium and sodium chlorides is in good agreement with Fick's law, especially when the diffused salts are measured in gram-equivalents. From this law it follows that, when an aqueous solution diffuses into water and the whole column of liquid is divided at any moment into eight equally deep horizontal layers, each pair of layers equidistant from the middle will contain together one-fourth of the total solute. This result is in very close accord with the results of experiments on mixtures of the two above chlorides.

T. H. P.

**Effect of Interionic Forces on the Osmotic Pressure of Electrolytes.** SAMUEL R. MILNER (*Phil. Mag.*, 1913, [vi], **25**, 742-751).—In a previous paper (*Ibid.*, 1912, [vi], **23**, 551) it has been shown that a completely dissociated mixture of ions possesses a finite virial. In applying this result to solutions, it follows that the osmotic pressure of the ions of an electrolyte differs from that of the undissociated molecules. By reference to the freezing-point data for dilute solutions of a number of binary electrolytes, it is shown that the observed lowering of the freezing point can be satisfactorily accounted for on the assumption that the electrolytes are completely ionised, and that the interionic forces have the effect of reducing the osmotic pressure below the value which would correspond with the simple gas law.

H. M. D.

**Miscibility of Liquids at Pressures up to 3000 Atmospheres.** PHILIPP KOHNSTAMM and JEAN TIMMERMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1021-1037).—An apparatus is described which has been employed in experiments on the influence of pressure on the critical solution temperature of binary mixtures up to pressures of about 3000 atmospheres. The arrangement is such as to enable the phenomenon to be investigated by direct visual observation of the change which occurs in the nature of the system at the temperature in question.

The results obtained with the following pairs of liquids are recorded in tables, in which the values of  $dt/dp$  are indicated for the different pressure intervals—hexane and nitrobenzene, diisobutyl and nitrobenzene, American petroleum and nitrobenzene, cyclohexane and aniline, water and triethylamine, water and methyl ethyl ketone. The behaviour of these systems is quite in accordance with theoretical predictions, and the last-mentioned pair is of particular interest in that it represents a system in which the transition from a partly miscible to a completely miscible condition can be actually effected at constant temperature by a change in the pressure.

H. M. D.

**Binary Mixtures and Concentrated Solutions. III.** FRIEDRICH DOLEZALEK (*Zeitsch. physikal. Chem.*, 1913, **83**, 40-44).—Polemical answer to Patterson (*A.*, 1910, ii, 167) and van Laar's (*A.*, 1910,



ii, 583) criticism of the author's paper (A., 1909, ii, 22). It is shown that Patterson's objections rest mainly on a printer's error, and that the densities of the mixtures were calculated in the usual manner, and not as is suggested in Patterson's paper. The theory put forward by van Laar is shown to be opposed both to experimental facts and thermodynamical considerations (see also Dolezalek, A., 1910, ii, 184). J. F. S.

**Binary Mixtures and Concentrated Solutions. IV. The Mixture Ethyl Ether-Chloroform.** FRIEDRICH DOLEZALEK and A. SCHULZE (*Zeitsch. physikal. Chem.*, 1913, 83, 45-78. Compare A., 1909, ii, 22; 1910, ii, 184, and preceding abstract; also Dolezalek and Schulze, A., 1913, ii, 108).—The authors have studied the system ethyl ether-chloroform from the point of view of the Dolezalek theory of mixtures. It is shown that a complex compound is formed by ether and chloroform, which is made up of one molecule of ether and one molecule of chloroform. The conditions are such that the equilibrium  $C_2H_5O \cdot CHCl_3 \rightleftharpoons C_2H_5O.CHCl_3$  is set up and obeys the law of mass action. Naturally, the physical constants of such a mixture could not be calculated from the usual mixture laws. The molecular condition of the mixture is determined by the authors at temperatures 20–100°, and it is shown that with increasing temperature the dissociation of the molecular compound increases rapidly. By cautious cooling of an equilibrium mixture, it was possible to isolate the compound in the solid state, and to show that it melted at –80°, or 30° above the melting point of ether. It is also shown that on mixing unsaturated ether and chloroform vapours, a contraction occurs which at 50° and 1 kilo. per sq. cm. pressure points to the presence of 0.01 mol. of the compound in the vapour. The vapour-pressure curves of the ether-chloroform mixtures are convex to the concentration axis, nevertheless the values can be calculated over the whole concentration range by means of the law that "The partial pressure of each component of a mixture is equal to the saturation pressure of the pure component multiplied by the molecular fraction of this component in the liquid mixture." The vapour-pressure curve approaches the ideal straight line curve with increasing temperature, as it must do according to the theory, for with increasing temperature the compound dissociates, and it becomes potentially a mixture of two substances without action on one another. The heat developed on mixing chloroform and ether was measured, and from the values it was calculated that the heat of formation is about 3000 cal. The heat capacity of the compound is considerably greater than that of its components, since on heating, a considerable portion of the heat is used in dissociating the compound. It is shown that if the formation of the compound is considered, the specific heat of the mixtures for all concentrations can be calculated. On mixing ether and chloroform, a considerable contraction occurs, so that the density of the mixtures differs widely from the value calculated by the volume mixture law. But if the constitution of the mixture is calculated from the mass action constant and the

concentration of the three substances considered, the density can be calculated, which agrees well with the observed values. The coefficient of refraction for long wave lengths is determined, and the divergence of the values from those calculated by the Lorentz formula is shown to be due to the presence of the compound, and not, as has often been stated, to molecular attraction as represented by the van der Waal theory. The viscosity of mixtures is also considered, and it is shown from the values of Thorpe and Roger (T., 1897, 71, 373) that, although they in no sense agree with values calculated from a mixture formula, yet if the presence and amount of the compound is brought into the calculation, values are obtained with which they agree in the highest degree. In conclusion, the authors state that to portray the whole physico-chemical behaviour of an ether-chloroform mixture, it is sufficient to determine the vapour pressure for one single concentration, and to calculate the mass action constant from this. By means of this constant all the properties of the mixture over all concentrations can be calculated by the method given in the paper. J. F. S.

**Precipitation of Salts by the Corresponding Acids.** IRVING MASSON (*Proc. Roy. Soc. Edin.*, 1913, 33, 64-67).—The extent to which the solubility of salts in water is affected by the presence of the corresponding acids may be determined by solubility measurements or precipitation experiments. The relationship between the two methods is discussed, and it is shown that the "critical" concentration of acid ( $A$ ), which just fails to precipitate salt when a small quantity of the acid solution is added to a neutral saturated solution of the salt, is equal to the product of the solubility of the salt in pure water ( $B$ ), and the initial slope of the solubility-acidity curve ( $k_0$ ), that is,  $A = k_0 B$ . The data obtained for sodium and barium chlorides are in satisfactory agreement with this deduction, but there is an appreciable divergence between theory and experiment in the case of barium nitrate.

According to Engel's data for the solubility of the chlorides of the alkali and alkaline earth metals in water and hydrochloric acid solutions, it appears that  $k_0$  is approximately equal to unity in all cases. H. M. D.

**Chemical Significance of Crystalline Form.** THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1913, 35, 581-596).—In this paper, the author's theory of the compressibility of atoms (T., 1911, 99, 1207) is considered in its relation to the structure of crystals. Barlow and Pope's valency-volume hypothesis is discussed, and it is held that it does not afford the most reasonable explanation for the actual molecular volumes of solids. Some of the arguments advanced in favour of the approximate equality of the valency-volumes are just as valid in support of any other theory involving close-packing of molecules, and there are certain facts which seem quite beyond the reach of this hypothesis.

The present theory accords with all the crystallographic facts hitherto recorded. It assumes, like Barlow and Pope's hypothesis,

that the atoms in solids are closely-packed, and thus maintain the form and rigidity of the structure. It proposes, however, that the atoms are compressible, and that their volumes are not arbitrary, but depend on the pressure to which they are subjected. This theory affords a better explanation of the usual forms of elements and binary compounds than Barlow and Pope's, and also accounts for the fact that elements forming isomorphous compounds need not have exactly the same atomic volume. It also furnishes a conception as to the manner in which potassium and ammonium can replace one another isomorphously, a problem which seems inexplicable on the constant valency-volume hypothesis. E. G.

#### Linear Velocity of Crystallisation of Isomorphous Mixtures.

MEINHARD HASSELBLATT (*Zeitsch. physikal. Chem.*, 1913, **83**, 1-39). Compare Tammann (A., 1897, ii, 414; 1899, ii, 272, 518), Friedländer and Tammann (A., 1898, ii, 17), Bogojavlenski (A., 1899, ii, 206), Pickardt (A., 1903, ii, 66), Dreyer (A., 1904, ii, 611). The fusion curves of binary isomorphous mixtures, which give mixed crystals continuously over the whole range of concentrations were determined for the following pairs: Cadmium nitrate tetrahydrate-calcium nitrate tetrahydrate; *m*-chloronitrobenzene-*m*-bromonitrobenzene; *m*-chloronitrobenzene-*m*-iodonitrobenzene; *m*-bromonitrobenzene-*m*-iodonitrobenzene; *m*-bromonitrobenzene-*m*-fluoronitrobenzene; and *m*-chloronitrobenzene-*m*-fluoronitrobenzene. For the mixture, cadmium nitrate-calcium nitrate, it is shown that mixed crystals are formed only with the unstable variety of calcium nitrate; the melting points of the mixtures lie between those of the two components without showing either maximum or minimum melting points. In the mixtures of the halogen nitrobenzenes, the pair *m*-bromonitrobenzene-*m*-chloronitrobenzene show no minimum melting point, whilst all the other pairs do. The velocity of crystallisation of the above-mentioned pairs of substances is determined, and this quantity is generally between that of the pure substances, except more especially in the case of the mixtures containing the fluorine derivatives, where a minimum is observed. The velocity of the transition of the unstable variety of calcium nitrate into the stable variety is measured. It is shown that in the case of each of the halogen derivatives of nitrobenzene an unstable variety exists; the melting points of these are determined, and have the following values:

	$\text{C}_6\text{H}_5\text{F}\cdot\text{NO}_2$	$\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$	$\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$	$\text{C}_6\text{H}_4\text{I}\cdot\text{NO}_2$
Stable .....	33.1	41.6	51.6	53.6
Unstable ...	4.1	21.9	17.5	22.6

It is thought to be likely that other unstable modifications are also capable of existence.

The systems azobenzene-benzylideneaniline; benzylideneaniline-benzylaniline were examined, and shown not continuously to produce mixed crystals, but to give eutectic mixtures. This fact is in opposition to the various results in the literature. In agreement with Bogojavlenski and Sacharov, it is shown that the velocity

of crystallisation changes with the concentration, and that in the heterogeneous region it is very small. The maximum velocity of crystallisation is shown to occur at 25–30° supercooling in the same way as for pure substances. The relationship between the velocity of crystallisation and the cooling bath temperature is of the same nature as that for pure substances. If one component of an isomorphous binary mixture is abnormal, the mixture takes up a mean position between the two substances. In some cases the temperature at the crystallisation surface exerted considerable influence on the maximum crystallisation velocity, whilst in other cases it is without influence. In the latter case the velocity of crystallisation is additive, and the curves are thereby caused to lie below the straight line. With mixtures which do not form mixed crystals in all proportions it is shown that the velocity of crystallisation decreases very much, although in these cases the decrease is less than in the case of substances which do not form mixed crystals at all. The velocity of crystallisation in cases of substances which only form mixed crystals over certain concentrations is very variable, owing to the concentration differences in the still liquid mixture.

J. F. S.

**Colloidal Sulphur.** SVEN ODÉN (*Nova Acta Regiae Soc. Sci. Upsala*, 1913, [iv], 3, 1–193).—A detailed account is given of the author's work on the preparation, purification, and physical properties of colloidal solutions of sulphur, and on the phenomena associated with the coagulating action of electrolytes. Many of the observations have been published previously (*A.*, 1911, ii, 388, 971; 1912, ii, 249, 1143).

In regard to the conditions which are favourable to the formation of colloidal sulphur, the observations indicate that the most important factor is a high concentration of the substances, by the interaction of which sulphur is set free. Although low temperatures have been stated to be favourable to the production of colloids, this is contrary to the author's experience, for experiments on the interaction of 3*N*-sodium thiosulphate solution with concentrated sulphuric acid, at temperatures between –5° and +35°, gave a maximum yield of colloidal sulphur at 25°.

The physical properties examined were the density, thermal expansion, viscosity, surface tension, diffusibility, refractivity, osmotic pressure, and colour.

From the behaviour of colloidal sulphur towards electrolytes, it would appear that the phenomena of coagulation can in general be more satisfactorily interpreted in terms of Freundlich's theory as compared with the various other theories which have been put forward up to the present.

H. M. D.

**Validity of the Boyle-Gay-Lussac Laws for Colloidal Solutions.** III. ARNE WESTGREN (*Zeitsch. physikal. Chem.*, 1913, 83, 151–195. Compare *A.*, 1910, ii, 772; 1911, ii, 703).—The present paper is a continuation of the work of Svedberg, and deals chiefly with the relationships between the compressibility, concentration, and size of the particles. The measurements are made by

a method differing but slightly from that described by Svedberg (*loc. cit.*). The substances employed in the present experiments were sols of mercury, sulphur, and selenium, and emulsions of castor oil and wool fat. Four different mercury sols were employed, prepared as follows: (1) By precipitation of a 0.25 mol. solution of mercuric chloride in 0.9% gelatin by a drop of sodium hydroxide solution, and then reduction with a few drops of hydrazine hydrate solution, the diameter of the particles was  $53\mu$ ; (2) electric formation by means of an arc between mercury and iron, the diameter of the particles was  $69\mu$ ; (3) as (2), except that a gelatin solution was used instead of water, the diameter of the particles was  $137\mu$ ; (4) by precipitation of a 5% mercuric chloride solution by sodium hydroxide, and reduction of the mercuric oxide by hydrazine, the diameter of the particles was  $190\mu$ . Four sulphur sols were employed, the particles of which had diameters  $140\mu$ ,  $164\mu$ ,  $278\mu$ , and  $358\mu$ . Four selenium sols were used, the particles of which had diameters  $107\mu$ ,  $132\mu$ ,  $181\mu$ , and  $242\mu$ . The castor oil emulsion particle had diameters  $316\mu$ , and the wool fat emulsion  $212\mu$ . From a very large number of observations it is shown that the curve representing the relation between  $\beta/\beta_0$  and the number of particles for mercury sols is very like that for gold sols. In the case of sulphur sols and the emulsions the compressibility relationship ( $\beta/\beta_0$ ) is a linear function of the concentration. The selenium sols take up a position intermediate between that of gold and gamboge. From the curves for sols of gold, mercury, and sulphur, it is shown that the product of the diameter of the particles ( $d$ ) and the concentration of the sol ( $c$ ) is constant, and that  $\beta/\beta_0 = 1 - \text{const.} \cdot c$ . The relationship between the compressibility ratio and the specific gravity ( $s$ ) of the dispersed substance is given by  $\beta/\beta_0 = 1 - \text{const.} \cdot s$ . From the two equations, the relationship between the compressibility ratio, diameter of the particles, concentration, and specific gravity is given by the expression  $\beta/\beta_0 = 1 - \text{const.} \cdot d^2 \cdot c$ . J. F. S.

**The Theory of Intra vitam Staining.** RUDOLF HÖBER and OTTO NASR (*Biochem. Zeitsch.*, 1913, 50, 418-436).—The theory of Ruhland (A., 1909, ii, 257), according to which the staining capacity of a dye is a function of its dispersion grade in solution, is criticised. The authors draw the conclusion that this theory cannot be substantiated, either for acid or basic dyes. It does not explain, for example, why certain highly dispersed acid dyes are not taken up by numerous animal and vegetable cells, although it is possible that dyes cannot be taken up when their dispersion grade is below a certain limit, and they are readily precipitated by small dilutions of salts. The permeability cannot therefore be explained simply as a filtration process where the plasma membrane acts as an ultra-filter. S. B. S.

**The Relationship between Colloid Coagulation and Adsorption and the Velocity of Coagulation.** N. ISHIZAKA [and, in part, HERBERT FREUNDLICH] (*Zeitsch. physikal. Chem.*, 1913, 83, 97-128).—The object of the present paper is to show that the relationship

between coagulation by electrolytes and adsorption, which was found to hold by Freundlich (A., 1910, ii, 692) for  $\text{As}_2\text{S}_3$  sols, also hold for aluminium hydroxide sols. The  $\text{Al}(\text{OH})_3$  sol was prepared according to the method of Crum (Lundén, 1851, 89, 156), and the alumina used for the adsorption experiments was "grown alumina," that is, such prepared by rubbing aluminium foil with mercury. The adsorption of the salts, sodium chloride, potassium chloride, ammonium chloride, potassium thiocyanate, potassium nitrate, potassium sulphate, potassium chromate, potassium dichromate, potassium ferrocyanide, potassium salicylate, potassium oxalate, potassium sulphanilate, and potassium succinate was determined with alumina, and the change in the concentration of the anion determined. The adsorption isothermal  $\alpha = \alpha c^{1/n}$  held in every case. The coagulation value of  $\text{Al}(\text{OH})_3$  sol was determined for the same salts. The method adopted for obtaining this value was to determine the electrolyte concentration which produced a given change in the viscosity of the sol in a given time. In accord with the Freundlich theory, it is shown that those anions which have a strong coagulating action are also strongly adsorbed, and those which are weakly coagulating, for example, the univalent inorganic anions, are also only slightly adsorbed. The inorganic anions are not equally adsorbed from equivalent solutions, as is the case for inorganic cations, but the bi- and ter-valent anions were more strongly adsorbed. The coagulations values of the uni- and multi-valent ions show an even greater difference. The adsorption of the  $\text{Al}(\text{OH})_3$  particles on coagulation were measured in several instances, and here also the adsorption isothermal held. The course of the coagulation with time was followed by measuring the viscosity of the sol, to which the electrolyte had been added, from time to time. The results agree with those obtained by Paine (A., 1911, ii, 337) for the copper sol. It is shown that the results and also those of Paine, as expressed in the coagulation-time curve, can be obtained by means of the formula:

$$k = 1/2(1+h)/b' \{ (1-h) \log_e (1-hx) - \log_e (1-x) \} + x^2(1-x),$$

in which  $x$  is the amount coagulated, the total quantity being taken as unity,  $t$  the time,  $b$  and  $b'$  constants, of which  $b$  is a function of the electrolyte concentration and  $b'$  a function of the inflexion point of the curve. The coagulation constant  $k$  is related to the electrolyte concentration by the expression  $k = \lambda c^q$ , and between this expression and that of Paine,  $V = Le^p$ , the following relationships exist:  $k = 1/12 \lambda$ ;  $A = kL^2$ ; and  $q = 2p$ , where  $k$  is a proportionality constant. It is further shown that the maximum viscosity of a coagulated sol increases with its content of colloidal particles, but in the case of large content the increase is somewhat larger. The maximum viscosity depends in a degree on the nature of the coagulating electrolyte. The lyotropic colloids are noticeable by the fact that the viscosity is smaller on coagulation by nitrate and thiocyanate anions than by sulphate and succinate anions. Shaking and other mechanical influences change the viscosity of concentrated sols. The adsorption of potassium dichromate by alumina, just as by carbon, causes a portion of the electrolyte to

change into chromate. A method for the quantitative estimation of small amounts of sulphanilic acid is worked out, and depends on the formation of an azo-dye. J. F. S.

**General Principles of Equilibria in Divided Systems.** RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1913, 35, 307—316).—The general conditions for heterogeneous equilibria, summarised in the ordinary phase rule, are only applicable to systems in which the different phases are not sub-divided. In the present paper, consideration is given to the principles of isothermal equilibrium in a divided system, that is, a heterogeneous system in which at least one of the phases is present in more than one region, regions being divided from the rest of the system by boundary surfaces at which an abrupt change of properties takes place. The number of degrees of freedom in a divided system is given by the equation  $f = c - r + e$ , where  $c$  is the number of components,  $r$  the number of regions, and  $e$  the least number of variables, of which the specification, together with the compositions, is necessary for the thermodynamical description of each region. For systems containing thermodynamically identical regions,  $r$  may be taken as the number of non-duplicated regions, and  $e$  the number of variables necessary for the thermodynamic description of these non-duplicated regions. For the case that the only division is into thermodynamically identical regions, the equilibrium rule assumes the form  $f = c - p + e$ , where  $p$  is the number of phases.

A special analysis of the equilibrium in systems containing non-identical regions of the same phase has shown that such regions must differ from each other in the value of at least two variables besides concentrations, that each new such region, put into an equilibrium system, introduces at least one new degree of freedom, and that the degrees of freedom thus introduced are not identical with those which the system already possessed.

Discussions are given of the conditions under which variables may be neglected, of the conditions in permanent systems which are not in equilibrium, and of metastable, stable, and indifferent equilibria. E. G.

**Equilibria in Dispersed Systems and the Thermodynamic Theory of Colloids.** RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1913, 35, 317—333).—Dispersed systems may be regarded as a special case of divided systems (preceding abstract) in which the degree of division of at least one of the phases, the dispersoid, has become so high that the properties of the system depend appreciably on the size or number of the dispersoid particles present. A study has been made of the conditions for thermodynamic equilibrium in such systems. The different variables are considered on which the free energy of a dispersoid and dispersing medium depend, and it is shown that for equilibrium all the particles of dispersoid must be of the same size, and that with either a positive or negative value of surface tension between the phases the equilibrium is metastable.

Several dispersed systems with positive or negative surface tension are discussed, and the equilibrium rule for divided systems (*loc. cit.*)

applied. It is suggested that a zero value of surface tension between the phases is necessary for the permanent stability of dispersed systems, and therefore for the permanent colloidal state. On this basis, colloidal solutions have the same number of degrees of freedom as "true" solutions. Many of the properties of lyophobic and lyophilic colloids can be explained on the assumption that the surface tension between a lyophobic dispersoid and its dispersing medium is positive unless the dispersoid particles are electrically charged, and that for lyophilic colloids the surface tension between undispersed dispersoid and dispersing medium is negative. E. G.

**Equilibria in Ternary Systems. II.** FRANS A. H. SCHREINERMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 853-867).—A theoretical paper in which the conditions regulating the equilibrium of ternary systems at constant pressure and varying temperature are examined. J. M. D.

**Equilibria in Ternary Systems. III.** FRANS A. H. SCHREINERMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 867-879. Compare preceding abstract).—The nature of the equilibria in a ternary system, which is characterised by the existence of a point with a minimum vapour pressure, is discussed in detail. H. M. D.

**Chemical Reactions and Radius of Curvature.** G. REBOUL (*Compt. rend.*, 1913, 156, 1376-1378. Compare this vol., ii, 303).—If two cylinders of copper of different radius are placed side by side in an atmosphere of some corroding gas at low pressure, the cylinder having the smaller radius of curvature is attacked first, and protects the other from attack until it is itself completely coated with a film of compound. Similarly raised points on a plate are attacked first, and at very low pressures may protect the surface of the plate for several centimetres round each point. W. G.

**Velocity of Decomposition of Ozone in Aqueous Solution.** VICTOR ROTHMUND and A. BERGSTÄLLER (*Monatsh.*, 1913, 34, 665-692).—The ozoniser used was constructed according to the Siemens-Berthelot principle, the six ozonising tubes being arranged, however, in series and not in parallel. By cooling the tubes with a mixture of solid carbon dioxide and acetone, the percentage of ozone in the oxygen used could be made as great as 25-30%.

The velocity experiments were all carried out at 0°, the authors having first proved that the only decomposition product of ozone is oxygen; no trace of hydrogen peroxide is formed in pure aqueous solutions, or of persulphuric acid in sulphuric acid solutions. The estimation of the amount of ozone present in the various solutions was made by adding the aqueous solution to a solution of potassium iodide containing excess of sodium carbonate, then acidifying with dilute sulphuric acid, and titrating the liberated iodine; special experiments showed that this method gave exact results.

The stability of ozone solutions decreases as the concentration of hydron increases, but there is no proportionality between this



concentration and the velocity of decomposition; in alkaline solutions ozone is very unstable. In acid solutions the velocity of decomposition, under apparently the same conditions, was found to be very variable; the cause of this variability could not be traced to the presence of a catalyst; in fact, such substances as copper sulphate, colloidal platinum, stannous sulphate, etc., did not act as catalysts. In alkaline solution the irregularities above-mentioned were not noticeable.

In the most strongly acid solutions investigated (0.01*N*), the reaction is approximately of the second order; in the weakly acid, and in the alkaline solutions, the order of reaction lies between the first and second. If the assumption is made that a mono- and a bi-molecular reaction are superposed on each other, the differential equation  $dx/dt = A(a-x)^2 + B(a-x)$  is obtained, where  $A$  and  $B$  are constants; this satisfies the experimental results, but still requires explanation. In acid solutions, the first term is the more important, whilst in weakly acid and alkaline solutions, the second term plays the greater part.

T. S. P.

**Hygroscopy of Salts.** JOSEF HABERMANN (*Zeitsch. anal. Chem.*, 1913, 58, 303-304).—The publication of Schuyten's paper on this subject (A., 1912, ii, 716) leads the author to state that he has been for some time engaged in the study of hygroscopic salts and will shortly publish the first part of his results.

Air of any constant degree of humidity is most readily obtained by the use of aqueous salt solutions (sodium chloride, sodium nitrate, and others).

L. DE K.

**Rate of Reduction of Mercuric Chloride by Phosphorous Acid.** GEORGE A. LINHART (*Amer. J. Sci.*, 1913, [iv], 35, 353-368). Compare Montemartini and Edigi, A., 1903, ii, 65.—Owing to the unsatisfactory nature of the results which have hitherto been obtained for the kinetics of the reaction between mercuric chloride and phosphorous acid, the author has carried out fresh experiments. By Ostwald's isolation method, it is shown that the reaction is of the first order with respect to mercuric chloride; the total reaction is of the second order compare Montemartini and Edigi, *loc. cit.*; also Garner, Foglesong, and Wilson, A., 1911, ii, 972), taking place in two stages, probably the following: (1)  $\text{HgCl}_2 + \text{H}_3\text{PO}_2 \rightleftharpoons \text{HCl} + \text{HgCl} + \text{H}_2\text{PO}_2$ ; (2)  $2\text{H}_2\text{PO}_2 + \text{HCl} + \text{H}_2\text{PO}_2 \rightarrow \text{H}_2\text{PO}_4 + \text{H}_2\text{PO}_3$ , reaction (2) being very rapid as compared with (1), so that the concentration of the phosphorous acid at any time  $t$  may be denoted approximately by  $(b - \frac{1}{2}x)$ , instead of  $b - x$ ,  $b$  being the initial concentration, since for every two molecules decomposed one molecule is regenerated.

The reaction is accelerated by hydron. If no hydrogen chloride is present at the outset, the velocity constant of the second order goes through a minimum, which is shown to be due chiefly to the formation of complexes between the mercuric chloride and hydrogen chloride liberated during the reaction. When hydrogen chloride

is present at the outset, the velocity constant of the second order increases continuously, which increase can be explained by the breaking down of the complexes with decreasing concentration, assuming that only the single molecules  $\text{IIHgCl}_2$  react with the phosphorous acid. Making this assumption, the author deduces the velocity equation:  $dx/dt = k(a - x/2)(b - x/2)(C + x)$ , where  $a$ ,  $b$ , and  $C$  are the respective concentrations of the mercuric chloride, phosphorous acid, and hydrogen chloride at the commencement of the reaction. With this equation concordant velocity constants are obtained.

T. S. P.

**Oxidation of Ferrous Salts.** F. R. EXXOS (*Proc. Camb. Phil. Soc.*, 1913, 17, 182).—The rate of oxidation of ferrous salts in aqueous solution and in absence of free acid has been investigated by bubbling air or oxygen through the solutions at a constant rate of about one litre in three hours. At  $60^\circ$ , the rate of oxidation of the chloride, sulphate, and acetate is represented approximately by the ratio 1:10:100. In the case of the sulphate, the reaction velocity is proportional to the partial pressure of the oxygen, and the reaction appears to be of the second order so far as the ferrous salt is concerned. From the experiments on the influence of temperature, dilution, and nature of the acid radicle, it is found that the oxidation depends on the non-ionised part of the ferrous salt.

H. M. D.

**Velocity of the Reaction between Sodium Thiosulphate and Sodium Bromoacetate.** ARTHUR SLATOR (*Zeitsch. physikal. Chem.*, 1913, 83, 256).—The author draws attention to the results of Krapivin (this vol., ii, 310), which agree with his own (T., 1904, 85, 1287; 1905, 87, 481); also Slator and Twiss (T., 1909, 95, 93). It is pointed out that the reaction between sodium thiosulphate and ethyl monobromoacetate takes place rapidly, and is suitable for use by students.

J. F. S.

**Hydrolysis of Esters of Substituted Aliphatic Acids.** WILLIAM A. DRUSKUL and E. W. DEAN (*Amer. J. Sci.*, 1913, [iv], 35, 483—490. Compare A., 1912, ii, 927).—The rates of hydrolysis of the ethyl esters of lactic, glyceric, and  $\alpha$ - and  $\beta$ -ethoxypropionic acids have been compared at  $25^\circ$ ,  $35^\circ$ , and  $45^\circ$ , the experiments being made in dilute solution with 0.1N-hydrochloric acid as catalyst. The calculated velocity coefficients for  $25^\circ$  are as follows: Propionate, 71.6; lactate, 73.2; glycerate, 18.5;  $\alpha$ -ethoxypropionate, 19.7; and  $\beta$ -ethoxypropionate,  $11.3 \times 10^{-5}$ . The temperature-coefficient for the interval  $25^\circ$ — $35^\circ$  varies from 2.43 to 2.51.

From a comparison of the data for the propionate, lactate, and glycerate, it is evident that the substitution of the second hydroxyl group has a very much greater influence on the rate of hydrolysis as compared with the effect produced by the first. Although the lactate is hydrolysed somewhat more quickly than the propionate at  $25^\circ$ , the reverse holds at  $45^\circ$ .

H. M. D.

**Hydrolysis of Ethyl Acetate by Neutral Salt Solutions.** WILLIAM E. HENDERSON and DAVID R. KELLOGG (*J. Amer. Chem. Soc.*, 1913, **35**, 396—418).—It has been shown by Kellogg (A., 1909, i, 203, 627) that the rate of hydrolysis of ethyl acetate by water is greatly accelerated by potassium chloride, bromide, or iodide. In continuation of this investigation, the catalytic action of the chlorides of sodium, lithium, calcium, strontium, barium, and cadmium, and of cadmium iodide, has been studied at 100°. Conductivity and viscosity data have been obtained for these salts at concentrations and temperature employed in the hydrolysis experiments, and from them the degree of ionisation has been calculated.

The results show that the accelerating effect of lithium chloride is greater than that of sodium chloride, whilst the degree of ionisation is less, and that the chlorides of calcium, barium, and strontium have a greater effect than either sodium or potassium chloride, although they are less ionised. Cadmium chloride, the least ionised of any of the chlorides studied, produces the greatest effect, whilst cadmium iodide, which is less ionised than any of the other salts, produces the greatest effect of all.

It is evident that the effect produced by a neutral salt on the hydrolysis of ethyl acetate is due to a specific influence of the non-ionised portion of the salt rather than to any function of the ions.

E. G.

**Rate of Conversion of Cinchonine into Cinchotoxine.** HENRY C. BIDDLE and EDWIN ROSENSTEIN (*J. Amer. Chem. Soc.*, 1913, **35**, 418—426. Compare A., 1912, i, 296).—This investigation was undertaken with the object of devising a quantitative method for studying the transformation of alkaloids into their toxic isomerides, which should be more accurate than the ether extraction method employed previously. Two methods are described, one gravimetric, and the other polarimetric, and these have been applied to the determination of the specific reaction velocity of the conversion of cinchonine into cinchotoxine by the catalytic action of acetic acid.

The reaction has been found to be unimolecular with respect to the alkaloid, and the catalysis unimolecular with respect to undissociated acetic acid. The acetate ion has little or no influence on the rate of reaction, and the retarding effect of hydrogen ions at low concentrations is very small.

E. G.

**The Rate of Extraction of a Protein (Salmine) from Dissociated Tissue by an Aqueous Solvent.** T. BRAYSHAW ROBERTSON (*J. Biol. Chem.*, 1913, **14**, 237—249). The rate of extraction of salmine from dried fish spermatozoa by dilute acid is expressed by the formula  $x = Kt^m$ , where  $x$  is the amount extracted,  $t$  the time, and  $m$  and  $K$  are constants. The rate is determined by colligative forces. The accompanying chemical phenomena (decomposition of compounds of salmine within the tissue, formation of soluble chloride, etc.) occur at a relatively great velocity, and hence do not affect the rate of extraction.

W. D. H.

**Atomic Weight Estimation from Special Groupings of the Hydrides.** FREDERICK H. LOISING (*Chem. News*, 1913, 107, 193).—The fact that the molecular weights of the hydrides vary in a linear manner with the position of the contained elements in the periodic table is suggested as affording a means of fixing approximately the values of the atomic weights of certain elements. H. M. D.

**General Characters of the Actions between Atoms.** MARCEL BRILLOUIN (*Ann. Chem. Phys.*, 1913, [viii], 28, 567–577. Compare A., 1913, ii, 193).—The discussion commenced in the first paper (*loc. cit.*) is continued and extended to the consideration of valency, the mechanical explanation of which is shown to be difficult. Organic radicals are then dealt with, and it is suggested that radicals of the same valency are characterised by the existence of an external field of force, determined solely by the valency, and independent of the chemical constitution of the radical. An attempt is then made to define precisely the field of force acting on an atom, the action between two or more atoms, and, finally, the conditions of saturation. From these investigations the conclusion is drawn that a univalent atom cannot be isotropic, and cannot be regarded as a point. T. A. H.

**The General Theory of Valency.** HUGO KAUFFMANN (*Zeitsch. anorg. Chem.*, 1913, 81, 83–96). Certain conclusions from the theory of subsidiary valencies have been tested by optical means. Methoxyl increases the basic character of distyryl ketone, and deepens the colour of its salts. The dimethylamino group is a stronger auxochrome than methoxyl, and the basicity of tetramethylaminodistyryl ketone is actually much greater, but the colour of its salts is lessened, and in an excess of dilute acids even colourless salts are obtained. This apparently anomalous result is due to the formation of internal salts. Weak auxochromes have a greater effect on halochromy in concentrated sulphuric acid than strong auxochromes. The halochromy is governed by the capacity of the auxochrome to gather to itself valencies of hydrogen. Acetylation deepens the colour observed in the halochromy of amino derivatives. This effect has been studied in a number of cases. C. H. D.

**Radioactive Changes and the Valency Question from the Point of View of Atomic Structure.** KASIMIR FEMANS (*Ber. Deut. physikal. Ges.*, 1913, 15, 240–259).—The simple relation between the radioactive changes and the chemical character of the resulting elements appears to be conclusive in favour of the view that radioactive change is concerned with the same region of the atom as chemical phenomena. The periodic system is supposed to indicate generic relations between all the elements, and the most natural supposition is that they are produced by the continuation of the three known radioactive series, and that each element consists of at least three non-separable elements ("Ploid"). In attempting to continue these series the question arises whether the two end products of the thorium series, for example, can be identical, for the

energy content of the atoms must be different. The relative poverty of thorium minerals in lead as compared with those of uranium is explained by the smaller life-period of "thorium lead" than that of "uranium lead." It is necessary to suppose that, in addition to helium, at least a second atomic constituent exists, and this is taken to be hydrogen. Helium and hydrogen atoms are supposed to exist in the outer regions of heavy atoms, and the valency of the atom is conditioned by the power of these helium and hydrogen atoms to lose two or one electron respectively. In the group of rare earth elements, the evolution is regarded as being conditioned by the expulsion of singly charged hydrogen atoms rather than of helium atoms, producing an oscillation of the resulting elements between the third and fourth groups of the periodic table. A connexion between the age of minerals, their content of rare earth elements and the amount of hydrogen contained is indicated, and also the possibility that the rare-earth elements may be found to generate hydrogen in detectable quantities. Further, it is supposed that the change in the rare-earth group,  $A \xrightarrow{H} B \xrightarrow{H} A'$ , may produce two similar but still separable elements  $A$  and  $A'$ , whereas in the radio-elements in which helium is expelled instead of hydrogen, the elements are non-separable. In the VIII group something of the same sort may occur.

In explanation of  $\beta$ -ray changes, with increase of maximum valency by one unit, it is supposed that a helium atom arrives at the surface of the atom from its interior, and exchanges places with a hydrogen atom. The relation of these views to other structural theories is discovered. F.S.

**Relation of the Value of "a" of van der Waals' Equation to the Molecular Weight and the Number of Valencies of the Molecule.** ALBERT P. MATTHEWS (*J. Physical Chem.*, 1913, 17, 183—201). Compare this vol. ii, 300.—The author has already deduced that  $a = N^2 M^2 K$ , where  $N$  is the number of molecules in one c.c. of gas under standard conditions,  $M$  the mass of cohesion of a molecule, and  $K$  a constant, and that  $M^2 K$  is related to the surface tension. The function  $M^2 K$  is also related to the molecular weight  $H$  and the sum of the valencies in the molecule  $Z$  by the empirical equation,  $M^2 K = 2.98 \times 10^{-37} (H/Z)^{2/3}$ , so that  $a = 2.256 \times 10^{-4} (H/Z)^{2/3}$ . The value of the constant, 2.98, is the mean of the values given by 26 non-associating substances of which the critical data were determined by Young, the extreme values being 2.73 and 3.09. A similar value was obtained from forty-five other substances, the critical data of which are not so well established.

Associating substances, including hydrogen chloride, give a higher value than 2.98, but a number of simple gases, such as nitrous oxide, chlorine, etc., behave normally when suitable valency numbers are chosen. Thus chlorine in  $Cl_2$  is supposed to be trivalent, oxygen in  $O_2$  univalent, and carbon in  $CO_2$  bivalent. Substances of low molecular weight and great simplicity, such as hydrogen and methane and substances of high molecular weight, such as

diphenyl, also give abnormal values of the constant. This is possibly because the accepted values of  $a$  are incorrect.

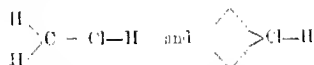
The close approximation of the constant to the figure representing the gravitational attraction of two average molecules, namely,  $3.11 \times 10^{-37}$ , is regarded as a coincidence.

R. J. C.

**Valency of Chlorine as Determined from the Molecular Cohesion of Chlorine Compounds.** ALBERT P. MATHIJS (*J. Physical Chem.*, 1913, **17**, 252–263. Compare preceding abstract).—The sums of the valencies in twenty-one compounds containing chlorine have been calculated from the critical data by means of the author's formula connecting  $a$  of van der Waals' equation and molecular cohesion with valency. The conclusion is drawn that chlorine is seldom or never univalent, but is certainly tervalent in most of the cases dealt with. This result finds support in Pascal's measurements of diamagnetism (1911) and Brude's theory connecting valency with absorption of light (1901).

Valencies are classified as "acting," "active but not acting," and "resting." Molecular cohesion is unaffected by resting or self-polarised valencies, but is affected equally by active and acting valencies. Active valencies are recognised by a tendency towards molecular association as in hydrogen chloride, but in non-associating substances all the valencies must be acting valencies.

The author gives structural formulae with "acting" tervalent chlorine for a number of well-known compounds. Some of these formulae are very unusual. Thus methyl chloride and chlorobenzene are represented as:



respectively. These formulae are claimed to have advantages over the usually accepted ones in explaining some of the properties of the substances represented.

The valency of bromine and iodine cannot be decided owing to the uncertainty of most of the critical data, but fluorine appears to be univalent in fluorobenzene.

R. J. C.

**Valency of Oxygen, Sulphur, Nitrogen, and Phosphorus Determined from the Molecular Cohesion.** ALBERT P. MATHIJS (*J. Physical Chem.*, 1913, **17**, 331–356. Compare this vol. ii, 1941).—The total valency in a number of esters, calculated from the critical data, indicates that one of the oxygen atoms is quadrivalent, as suggested by Stieglitz. The oxygen in several ketones, nitrobenzene, acetic anhydride, and ethyl acetate also appears to be quadrivalent, whereas in ether, sulphur dioxide, and carbon dioxide it is bivalent, and in carbon monoxide and gaseous oxygen univalent.

Sulphur is said to be quadrivalent in sulphur dioxide and sulphuryl chloride, and sexavalent in hydrogen sulphide and a number of other compounds, but in no case is it bivalent.

Nitrogen appears to be univalent in gaseous nitrogen as well as

in nitric oxide, whilst nitrous oxide, with a total valency of six, must be written  $\text{N}\cdot\text{O}\cdot\text{N}$  or  $\text{N}\cdot\text{N}\cdot\text{O}$ . In other compounds nitrogen is ter- or quinque-valent, according to the usual view.

In phosphine the valency of phosphorus is certainly greater than three, and possibly, in a few molecules, greater than five.

R. J. C.

**Valency of the Argon Group as Determined from the Molecular Cohesion.** ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, 17, 337—343. Compare this vol., ii, 494).—The elements of the argon group, being liquefiable, must have some molecular cohesion. It follows that they must have some valency, it having been shown that there is a close connexion between the two attributes. The valencies as computed from the critical data are as follows: Helium, 0.1; neon, 0.32; argon, 1.12; krypton, 1.23; xenon, 1.80. Using the values of  $a$  calculated from the surface tension, a similar set of valency numbers is obtained.

The author holds that valencies are necessarily integral, so that fractional values represent some kind of equilibrium. The following hypothesis is suggested in explanation of the fractional values. The elements of the argon group have no principal valency, but a pair of secondary valencies, one of which is positive and one negative. At any given moment only a certain proportion of the atoms have their secondary valencies unlocked. The proportions are: Xenon, 90%; krypton, 65%; argon, 60%; neon, 16%; helium, 5%. This decrease in the proportion of open valencies corresponds with a progressive decrease in the solubility of these gases in water.

R. J. C.

**The Nature of Auxiliary Valencies. IV. Metal Ammonias.** III. FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1913, 83, 196—226. Compare A., 1912, ii, 546; this vol., ii, 129, 130).—A continuation of the work on metallic ammonias of bivalent metals. The sulphates of the metals nickel, cobalt, iron, copper, manganese, zinc, mercury, tin, lead, calcium, strontium, and barium are examined as to their ammine derivatives. The temperatures are determined at which the hexammine or pentammine of the above-mentioned metals exhibit a pressure of ammonia of 500 mm., and it is found, except in the case of cadmium, that the larger the atomic volume of the metal the smaller the temperature. The metals mercury, tin, lead, calcium, strontium, and barium are not included in the above generalisation, since they do not form comparable ammonias. It is shown that the value  $\chi/T$  is constant when hexammines or pentammines of the sulphates of bivalent metals are considered; it has a mean value of 13°. The value  $\chi/c \cdot \chi/T$  is also constant, and has a mean value of 365. Cadmium sulphate ammonias are exceptional to this, and have values 161 and 123 respectively. The physical meaning of the value  $\chi/T$  is critically considered. It is shown that those sulphates of bivalent metals which form hexammines do not form pentammines, and vice versa. The metals nickel, cobalt, iron, manganese, and cadmium form derivatives with

6, 4, and 2 molecules of ammonia, those of copper with 5, 4, and 2, and those of zinc with 5, 4, and 3 molecules of ammonia. The heat of dissociation of the various amines is calculated by means of the formula  $\log p = -Q/4571T + 1.75T - 3.3$ . The modulus of the ratio between the dissociation pressure of the iodide and corresponding sulphate at a series of temperatures is calculated for the metals nickel, cobalt, iron, manganese, cadmium, and zinc. This value is very constant, and for the first four metals has a value about 1.22, whilst for the two latter the value is about 1.05—1.13. Measurements of pressures are also given for lead iodide, bromide, and chloride, and for cupric chloride. Finally, measurements are given for an isomorphous mixture of nickel and cobalt chlorides in equal proportions by weight. The values are considerably changed from those of the pure substances.

J. F. S.

**The Nature of Auxiliary Valencies.** FRITZ FRIEDRICH (*Zeitsch. physikal. Chem.*, 1913, 83, 242—244).—Polical against Ephraim (this vol., ii, 130). It is shown that in the case of insoluble solutes no transition point is to be expected; that the differences stated by Ephraim to exist between hydrates and amines are due to the fact that he compared insoluble amines with soluble hydrates without considering the influence of solubility on the dissociation curve; and finally it is shown that hydrates and amines are analogous in every possible way.

J. F. S.

**The Importance of Symmetry in the Systematics of Chemical Compounds.** A. SCHLEICHER (*Zeitsch. anorg. Chem.*, 1913, 81, 97—101).—Theoretical.

C. H. D.

**New Supports for Burettes and Funnels.** A. BOUCHONNET (*Bull. Soc. chim.*, 1913, [iv], 13, 160—164).—To the base of these supports a copper rod is fixed, which fits inside a copper tube bearing a disc of opal glass and an adjustable casting, to which four simple clamps for burettes, or four bevelled rings for funnels or two of each are attached. The vessels may therefore be rotated with the receivers which are placed beneath them on the glass disk, or, by loosening the screws which fix the clamps to the stem, the disk may be moved independently.

J. C. W.

**An Apparatus for Extraction of Solids and Liquids.** HANS AROX (*Biochem. Zeitsch.*, 1913, 50, 386—387).—Two forms of apparatus for extraction respectively of solids and liquids are figured. A wide glass mantle is ground into a wide-mouthed flask, which contains the liquid used for extraction. The upper part of the mantle is narrowed, and connected with the inner tube of a condenser. Into the wide end of the mantle, the syphon apparatus is introduced and suspended from hooks in the upper part of the mantle. The latter differs in form according to whether the apparatus is employed for extraction of solids or liquids. The advantage claimed is that the substance extracted is continually surrounded by the boiling vapours of the liquid used for extraction.

S. B. S.



**Apparatus for the Recovery of Solvents in the Evaporation of Solutions.** WALTHER FRIESE (*Pharm. Zentr.-h.*, 1913, 54, 419-420).—The apparatus consists essentially of two parts: a double-walled, inverted funnel-shaped vessel, through which cold water can be circulated; and a glass or metal annular trough, in which the above vessel rests on three supports. This trough is also provided with a tube for removal of condensed solvent.

In use, the trough is laid on the rim of the crystallising or evaporating dish, which is heated on the water-bath. The vapours of the solvent, mixed with some water vapour, are condensed on the sides of the funnel, from which they flow into the trough, and thence into a suitable receiver. A quantitative recovery of the solvent is not claimed.

H. W.

## Inorganic Chemistry.

**Simple Apparatus for Catalytic Reductions with Hydrogen** HUGO VOSWICKEL (*Chem. Z.-t.*, 1913, 37, 489).—The apparatus consists of two glass bottles of 1000-1500 c.c. capacity, each of which is provided with a side tubulure at the bottom. They are connected with each other by means of a piece of glass tubing passing through the tubulures, and the neck of each bottle is fitted with a rubber bung, glass and rubber tubing, and screw-clip. About 1000-1500 c.c. of water is placed in the bottles, and then pressure applied to the one bottle (*A*) until the other (*B*) is full of water. *B* is then connected to the hydrogen cylinder and filled with hydrogen, *A* at the same time becoming filled with water. *B* is then connected to the apparatus where the catalytic reduction is to take place, and *A* to the hydrogen cylinder, the valve of which is regulated to give the necessary pressure. When all the hydrogen in *B* has been used up, *A* has become full of hydrogen, and *B* of water; it is only necessary then to reverse the apparatus, and so on.

T. S. P.

**Action of Some Organic Acids on the Decomposition of Hydrogen Peroxide.** C. POMAZZA and G. NONZI (*Atti R. Acad. Lincei*, 1913, v. 22, i, 238-245).—The decomposition of hydrogen peroxide is considerably accelerated by the presence of small quantities of manganous sulphate in neutral solution. The decomposition of hydrogen peroxide is retarded by uric acid, and even more by oxalic acid, hippuric acid, and benzoic acid.

R. V. S.

**Studies in Oxidation.** HENRY E. ARMSTRONG and REGINALD T. COLGATE (*J. Soc. Chem. Ind.*, 1913, 32, 394-397). The paper is divided into the sections: (*a*) The Nature of the Process; (*b*) Passive Metals; (*c*) Higher Metallic Oxides; (*d*) Oxidation by Permanganate; (*e*) Oxidation of Carbon; and deals with the application

of one of the author's (H. E. A.) well-known views on the mechanism of the process of oxidation to the above cases (compare T., 1903, 83, 1088; A., 1905, ii, 448). The behaviour of various metals in the presence of hydrogen peroxide and acids, when functioning as anodes, is described, the results indicating that higher unstable oxidation products are formed, which may play a part in the phenomenon of passivity. The views of Veley, with respect to the action of nitric acid on copper, of Wieland (A., 1912, ii, 347) on combustion, and of Rhead and Wheeler (T., 1912, 101, 846) are criticised.

T. S. P.

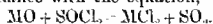
**The System Sulphur.** ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1913, 83, 221—241. Compare A., 1912, ii, 40).—The first part of the paper deals with a consideration of the occurrence of two liquid layers when sulphur is suddenly cooled to below  $170^{\circ}$  (compare Smith and Holmes, A., 1903, ii, 139, 284; 1905, ii, 382, 589; 1906, ii, 157; Malus, A., 1901, ii, 131; and Krut, A., 1908, ii, 1028). Krut and Bakhuis Roozboom were of the opinion that the formation of two layers pointed to a liquid transition point or the separation of both forms of sulphur in different layers. The author has carried out experiments which confirm the view of Smith, namely, that the two layers are due entirely to density differences of molten sulphur at different temperatures, the different temperatures being due to the poor conductivity for heat of the sulphur. It is thus made quite clear that no transition point occurs in the liquid phase. The second part of the paper is theoretical, and deals with the production of a  $T_x$  diagram for sulphur. The consideration leads to the conclusion that sulphur is certainly a ternary, and not a binary, system. The influence of the addition of  $S_R$  to equilibrium masses of  $S_B$  and  $S_H$  are considered under many conditions, and experiments are quoted which confirm the results theoretically observed. The diagram finally arrived at is drawn on the sides of a trigonal prism, and represents, according to the author, the simplest arrangement and a first attempt to produce such a diagram. The real diagram is probably much more complicated.

J. F. S.

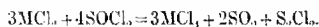
**Action of Thionyl Chloride on the Oxides of Metals and Metalloids.** HENRY B. NORTH and A. M. HAGEMAN (*J. Amer. Chem. Soc.*, 1913, 35, 352—356). Investigations have already been made of the action of thionyl chloride on selenium dioxide (Leather and North, A., 1907, ii, 255), tellurium dioxide (Leather and Hill, A., 1908, ii, 484), and on mercuric oxides (North, A., 1910, ii, 296). Darzens and Bourion (A., 1911, ii, 878) have studied its action on certain oxides, particularly those of the rare earth metals.

Experiments have now been made on the behaviour of thionyl chloride with zinc oxide, cadmium oxide, arsenic trioxide, antimony trioxide, bismuth trioxide, ferric oxide, glucinum oxide, calcium oxide, strontium oxide, magnesium oxide, silver oxide, cupric oxide, cuprous oxide, aluminium oxide, chromic oxide, and tin dioxide. These experiments were carried out in sealed tubes at  $150$ — $200^{\circ}$ .

In general, the action of thionyl chloride on a metallic oxide takes place in accordance with the equation,



In the case of a metal which has two oxides, the lower oxide when treated with an excess of the reagent is first converted into the lower chloride, and this is then oxidised to the higher chloride, thus:



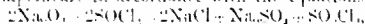
Arsenic trioxide yields only the trichloride. Antimony trioxide reacts at the ordinary temperature to form the trichloride, but when it is heated with excess of the reagent, the pentachloride is produced. Glucinum, calcium, strontium, and aluminium oxides, chromic oxide, and tin dioxide are not attacked by thionyl chloride at temperatures up to 200°. Silver oxide is but very slightly affected, only a trace of the chloride being produced. E. G.

**Some New Reactions with Thionyl Chloride.** HENRY R. NORTH and A. M. HAGEMAN (*J. Amer. Chem. Soc.*, 1913, **35**, 543--546).

--In an earlier paper (preceding abstract) an account has been given of the action of thionyl chloride on certain oxides. It has now been found that the peroxides also react with this reagent, and that sulphuryl chloride is invariably one of the products.

When barium peroxide is heated with a large excess of thionyl chloride in a sealed tube at 150°, the reaction proceeds thus,  $BaO_2 + 2SOCl_2 = BaCl_2 + SO_2 + SO_2Cl_2$ , but when the reagents are present in molecular proportions, the following reaction occurs:  $2BaO_2 + 2SOCl_2 = BaCl_2 + BaSO_4 + SO_2Cl_2$ . By varying the amounts of the reagents, a combination of the two reactions can be obtained. Barium oxide is not attacked by thionyl chloride at 150°. Lead dioxide and manganese dioxide react in the same way as barium peroxide.

Sodium peroxide reacts violently with thionyl chloride at the ordinary temperature in accordance with the equations



and  $Na_2O_2 + 2SOCl_2 = 2NaCl + SO_2 + SO_2Cl_2$ , depending on the proportions in which the reagents are used. E. G.

**Determination of the Atomic Weight of Selenium.** PHILIP BRYCLANTS and A. BYTHERIK (*Bull. Acad. roy. Belg.*, 1912, 856-859).

--The method employed by the authors was to determine the density of hydrogen selenide by direct weighing; the compressibility of the gas at 0° was also determined by essentially the same method as that used by Gray and Bart (T., 1909, **95**, 1633) in their experiments with hydrogen chloride. In determining the weight of a litre of the gas under normal conditions at Louvain, the gravimetric correction was made by comparison with the weight of a litre of oxygen determined under the same conditions. The result gave 3.6715 grams as the weight of the litre of hydrogen selenide, the error being 3 parts in 10,000. The atomic weight of selenium was found to be 79.48.

The only satisfactory method for the preparation of the hydrogen selenide used was by the action of water on aluminium selenide (compare Founes-Diacon, A., 1907, ii. 164). The gas was dried with phosphoric oxide, and condensed in a freezing mixture of solid carbon dioxide and ether. It was purified by distillation and sublimation, and when dry did not attack mercury so long as air was excluded.

T. S. P.

**The Reaction of Metals and Alloys with Nitric Acid.** JOHN H. STANSBIE (*J. Soc. Chem. Ind.*, 1913, 32, 311—319).—The investigation is a continuation of previous work (A., 1908, ii. 497; 1909, ii. 403), and deals with the metals copper, arsenic, zinc, silver, and bismuth, and their alloys. The apparatus used was an improved form of that previously described. The results previously obtained with the copper-arsenic alloys (*loc. cit.*) were confirmed by a fresh series of experiments; there seems to be an intimate connexion between the amounts of nitric oxide and nitrous acid formed during the reaction, a diminution in the volume of the former corresponding with an increase in the weight of the latter.

With alloys of copper and zinc, using nitric acid, D 1.149, and a temperature of 65°, the amount of acid entering into reaction, using the same weight of alloy and same volume of acid in each experiment, gradually diminishes as the percentage of zinc increases. All the alloys containing copper give a steady evolution of nitric oxide; no nitrous oxide could be detected. All alloys containing zinc give rise to the formation of small quantities of ammonia.

The reactions of bismuth with nitric acid are very similar to those of copper, but under ordinary conditions the rate of solution is slower. If the amount of nitrous acid present in the nitric acid is made as small as possible, bismuth dissolves to a greater extent than copper, but when the nitrous acid is present in the usual proportions the opposite is the case.

In all the above experiments the metals and alloys were used in a finely powdered state; in the following experiments plates of the metals were used, the temperature being that of the room. The rate of solution of silver is considerably reduced by dilution of the acid; acid of density 1.060 has no action within twenty-four hours, although there is action after seventy-six hours. Nitrous acid accelerates the reaction. Approximately half the quantity of acid required to convert silver into its nitrate is converted into nitrous acid, which would be in accordance with Divers' equation:  $2\text{Ag} + 2\text{HNO}_3 = \text{Ag}_2\text{NO}_3 + \text{AgNO}_2 + \text{H}_2\text{O}$ ; very little gas is evolved during the reaction with acids varying in density from 1.060 to 1.101. Similar results were obtained with copper, except that more gas is evolved than in the case of silver, probably because the less stable character of copper nitrite enables secondary changes to take place more readily.

As the result of his experiments the author comes to the conclusion that the reactions, for example, in the case of copper, are best represented by the equations:  $3\text{Cu} + 6\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)(\text{NO}_2) +$

33

$3\text{H}_2\text{O} + 3\text{Cu}(\text{NO}_3)(\text{NO}_2) + 2\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O} + 2\text{NO}$ . In the reactions of metals and alloys with nitric acid it is necessary to take into account (1) the purity and physical and mechanical condition of the metal or alloy, (2) the purity and concentration of the acid, (3) temperature, (4) the accumulation of the products of reaction in the solutions.

T. S. P.

**Compounds of Sulphur and Phosphorus. VIII. Tetraphosphorus Trisulphide,  $\text{P}_4\text{S}_3$ , and a New Phosphorus Oxy-sulphide,  $\text{P}_4\text{S}_5\text{O}_4$ .** ALFRED STOCK and KURT FRIEDEMANN (*Ber.*, 1913, 46, 1380—1387).—Dry tetraphosphorus trisulphide is stable in the air (compare A., 1912, ii, 1166), but solutions in benzene or carbon disulphide become cloudy almost immediately on exposure to the air, giving gradually a yellowish-white, voluminous precipitate of the phosphorus oxy-sulphide,  $\text{P}_4\text{S}_5\text{O}_4$ . This compound is best prepared by drawing air, laden with carbon disulphide vapour, for twenty-four hours through a solution of tetraphosphorus trisulphide in carbon disulphide. The precipitate thus formed is washed by decantation with carbon disulphide, and freed from the latter first in a vacuum over phosphoric oxide, and then in a current of hydrogen; in all operations it is necessary rigidly to exclude moisture. The oxy-sulphide forms a yellowish-white, non-crystalline powder, D. 1.96, which is insoluble in the usual solvents, and is decomposed by heat; it shows incipient fusion at  $150^\circ$ , and melts at about  $250^\circ$  to a golden-yellow liquid. It is very sensitive towards moisture, deliquescing in the air as readily as phosphoric oxide.

Ozonised oxygen can be used in the preparation instead of oxygen, when the reaction is complete in half an hour, but there is a tendency to form more highly oxidised products.

A mixture of  $\text{P}_4\text{S}_3$  and sulphur, when heated at  $100^\circ$ , gives the compound  $\text{P}_4\text{S}_5$ , no matter how great the excess of sulphur. If the temperature is allowed to rise to  $130^\circ$  the heat of reaction further raises it rapidly to  $300^\circ$ , and  $\text{P}_4\text{S}_{10}$  is formed. The compound  $\text{P}_4\text{S}_5$  is also readily obtained by heating a mixture of  $\text{P}_4\text{S}_3$  and  $\text{P}_2\text{S}_5$  in the proportions of  $3\text{P}_4\text{S}_3 : 4\text{P}_2\text{S}_5$  for twelve hours at  $140^\circ$ — $150^\circ$ .

T. S. P.

**Applications of Positive Rays to the Study of Chemical Problems.** SIR JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1913, 17, 291. Compare A., 1912, ii, 885, 1029).—Two samples of gases obtained from the residues of liquid air have been examined by the positive ray method. The one sample containing the heavier gases was found to be a mixture of xenon, krypton, and argon, and there were no lines on the photograph unaccounted for. The lighter sample was found to contain helium, neon, and a new gas of atomic weight 22. From the relative brightness of the lines of neon and the new gas, it would seem that the quantity of the new gas present in air is much smaller than that of neon.

The second part of the paper deals with the investigation of a new gas of atomic weight 3, which is found to make its appearance

in discharge tubes under certain conditions. The gas is given out by various metals when these are subjected to bombardment by cathode rays, helium being also liberated during the first stage of the bombardment. The metals used were iron, nickel, zinc, copper, lead, and platinum. It was also found to be given off by calcium carbide.

H. M. D.

**The Absorption of Neon by the Electrodes of Luminescent Tubes.** GEORGES CLAUDE (*Compt. rend.*, 1913, 156, 1317—1320, *Compare A.*, 1911, ii, 602, 1987).—Neon exhibits a very marked resistance to absorption by the electrodes in luminescent tubes, whilst producing rapid cathodic volatilisation of certain metals without itself entering into this volatilisation. Small quantities of helium and nitrogen present in neon rapidly disappear when the discharge is passing, but small quantities of neon cannot be similarly removed from helium. Tubes thus freed from nitrogen, when submitted to a greatly increased current, become filled with a blue light, which is characterised by the appearance of a continuous spectrum with a strong ray in the green and a series of rays in the violet.

W. G.

**Experiments on the Alkali Metals.** LOUIS HACKSPILL (*Ann. Chim. Phys.*, 1913, [viii], 28, 613—696).—The preparation of cesium, rubidium, and potassium by heating the anhydrous chlorides with metallic calcium is described. When the mixture containing a large excess of calcium is carefully heated in an exhausted iron tube placed in an electric oven, it is found that the alkali metals can be obtained in pure condition in nearly theoretical yield. The products have been used in the investigation of the physical properties, including the density, the coefficient of expansion, the vapour pressure, the density of the saturated vapour, and the electric conductivity; in addition the action of the metals on water at low temperatures has been investigated. Corresponding experiments have also been made with sodium.

The densities of the metals at 0° are 0.9723, 0.859, 1.525, and 1.903 for sodium, potassium, rubidium, and cesium respectively; the coefficients of expansion in the solid state, 0.000216, 0.00025, 0.00027, and 0.000291; in the fused condition, 0.000274, 0.000283, 0.000333, and 0.000345; the percentage increase in volume on fusion, 1.50, 2.42, 2.28, and 2.32. From the coefficient of expansion ( $\alpha$ ), the critical temperature ( $T_c$ ) has been calculated from the equation  $\alpha = 1/(2T_c - T)$ , where  $T$  is the temperature at which the expansion is measured. The values so obtained are: sodium, 2025°; potassium, 1965°; rubidium, 1857°; cesium, 1627°.

In some experiments in which an attempt was made to determine the thermal expansion of the metals immersed in benzene, it was found that this hydrocarbon is acted on by cesium even at the ordinary temperature. Although no hydrogen is evolved during the reaction, the black, amorphous substance which is obtained corresponds with the formula  $C_6H_5Cs$ . This formula is supported by the fact that diphenyl is formed when the substance is acted on

by water or alcohol. It takes fire on exposure to air, and burns with a smoky flame. On heating in carbon dioxide, it decomposes with slight explosion; it reacts violently with chloroform, but is not acted on by carbon tetrachloride, ethyl ether, or pentane.

Measurements of the vapour pressure of the metals were made at temperatures between  $250^{\circ}$  and  $400^{\circ}$ , and the results obtained are plotted in the form of vapour-pressure curves. The volatility increases at all temperatures with increase in the atomic weight. The attempts to measure the density of the saturated vapours have not given very consistent results, but they suffice to show that the alkali metals in the state of vapour consist of mon-atomic molecules.

The electric conductivities of the metals were measured in the liquid state and also in the solid state at temperatures ranging from the melting point down to liquid air temperatures. The results seem to show that the ratio of the specific resistances in the solid and liquid states is in the case of all four metals practically 1.5.

In reference to the action of water on the metals at low temperatures, it was found that the reactivity appears to increase as the atomic weight increases. The lowest temperatures at which the action could be detected were:  $-98^{\circ}$  in the case of sodium,  $-105^{\circ}$  for potassium,  $-108^{\circ}$  for rubidium, and  $-116^{\circ}$  for cesium.

H. M. D.

**Solution of the Constituents of Alluvial Sands by Subterranean Waters.** F. DIXNEUR (*Bull. Soc. chim.*, 1913, [iv], 13, 381—391).—As the result of a series of experiments conducted with waters and sands collected in the valley of the Loire between Nevers and Sully-sur-Loire, the author finds that when rain or river water filters through or flows over sand in presence of carbon dioxide, it dissolves calcium carbonate, magnesia, silica, and alkali salts in proportions which are characteristic for a particular sand. If the waters flow over sand in presence of an insufficient quantity of carbon dioxide, they may deposit calcium carbonate, with a little magnesia, but no iron, alumina, silica, or alkali salts will be lost. Analyses of the sands used in these experiments are given, and particulars of the quantities of the soluble constituents in the waters used before and after their contact with the sands.

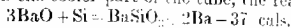
T. A. H.

**Determination of the Atomic Weight of Calcium.** WILLIAM ECHSNER DE COENCK (*Bull. Acad. roy. Belg.*, 1913, 222—223).—A weighed amount of pure precipitated calcium carbonate was treated with concentrated sulphuric acid. To the resulting precipitate and solution was added absolute alcohol, after which the calcium sulphate was collected on a tared filter paper, washed with absolute alcohol, and dried at  $100^{\circ}$ . The resulting atomic weights obtained were 40.16, 40.14, 40.13, 40.19, 40.11, giving an average value of 40.12 for the atomic weight of calcium.

T. S. P.

**Preparation of Barium.** CAMILLE MATIGNON (*Compt. rend.*, 1913, 156, 1378—1380. Compare following abstract).—Barium is

readily obtained by heating barium oxide (3 mols.) with silicon (1 atom) in a vacuum in a steel tube at 1200°. The metal distils off and condenses in the cooler part of the tube, the reaction being:



The silicon can be replaced by ferrosilicon containing 95% silicon.

W. G.

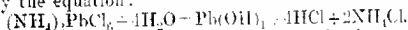
**Reduction of Magnesia by Aluminium.** CAMILLE MATIGNON (*Compt. rend.*, 1913, 156, 1157—1159).—Aluminium powder heated with heavy magnesium oxide in a vacuum at 1200° in a steel tube, readily and almost completely reduces the oxide, the magnesium being deposited in a crystalline state in the cool part of the tube.

W. G.

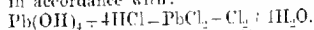
**Lead Tree in a Silicic Acid Gel.** ALFRED L. SIMON (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 171. Compare A., 1912, ii, 772).—The reduction of lead acetate in a silicic acid gel with the formation of a lead tree can be readily shown if a piece of zinc foil is supported with its lower edge below the surface of a gel prepared by mixing together a 15% solution of sodium silicate and a slight excess of 50% acetic acid, and then adding to the mixture about 10% of a concentrated solution of lead acetate. The solution is boiled to free it from carbon dioxide, and the zinc introduced into the cold solution.

H. M. D.

**Colloidal Lead Dioxide. Hydrolytic Method of Preparation.** ALEXANDER GUTHRIE and E. SAUER (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 171—177).—If small quantities of ammonium plumbichloride are added to a large volume of water, a brown, colloidal solution of lead dioxide is obtained. The reaction may be represented by the equation:



The solution is unstable, and soon becomes colourless as a consequence of the action of the hydrochloric acid, which is liberated, on the colloid in accordance with:



This may be prevented to a large extent if ammonia is added to the water in sufficient quantity to neutralise the acid which is subsequently set free. If, in addition, small quantities of gum arabic are dissolved in the water, it is possible to obtain fairly stable solutions of the dioxide. The best conditions are attained when 20 c.c. of N/5-ammonia solution are added to 250 c.c. of a 0.1% solution of gum arabic and 1 gram of the plumbichloride added gradually to the well-stirred solution. When freed from electrolytes by dialysis, the solution can be kept for a considerable time without much decomposition. On evaporation of the solution to dryness, the dioxide becomes insoluble.

The colloidal particles move to the positive pole in an electrical field. When mixed with hydrochloric and nitric acid solutions the brown colloidal solution is gradually decolorised, the velocity of the reaction increasing with the concentration of the acid. Sodium



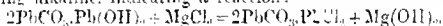
hydroxide has a similar action, but the change takes place much less rapidly. Sodium chloride, barium chloride, and aluminium sulphate have no coagulating action, and in presence of these electrolytes the dioxide appears to be approximately as stable as in pure water.

H. M. D.

**New Method for the Preparation of White Lead.** HANS HOR (*Zeitsch. anorg. Chem.*, 1913, 81, 40-45).—Lead sulphate dissolves in boiling concentrated magnesium chloride solution (mother liquors from potassium deposits), forming magnesium sulphate, which is readily extracted, and magnesium lead chloride. When impure lead sulphate from flue dust is used, copper and silver may be removed by immersing lead plates in the solution.

Magnesium oxychloride, prepared by adding the requisite quantity of milk of lime to magnesium chloride solution and boiling, is collected and mixed with an excess of water. Magnesium lead chloride is then added at 75-80° until the alkaline reaction disappears. The lead oxychloride is then allowed to settle, and the solution, which is now free from lead, is removed by decantation. A further quantity of moist magnesium oxychloride is now mixed with boiling water and saturated with carbon dioxide until the alkaline reaction disappears. The suspension of magnesium carbonate thus obtained is then run into the mixture of lead oxychloride and water, and stirred for an hour at 80°. The product has the composition  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ , and is completely amorphous.

White lead is completely dissolved in the cold, without decomposition, by a solution of magnesium chloride, D 1·16, the solution becoming alkaline, indicating a reaction:



C. H. D.

**The Electrochemical Production of Colloidal Copper.** T. ROLAND BRIGGS (*J. Physical Chem.*, 1913, 17, 281-319).—Allotropic copper first described by Schützenberger (A., 1878, 548), and more recently by Benedicks (A., 1907, ii. 548) presents many points of similarity to Carey Lea's gold-coloured allotropic silver, which is generally admitted to be colloidal. The author adduces evidence that Schützenberger's allotropic copper is, in fact, colloidal, and explains its formation on the protective colloid theory.

Copper acetate solution, particularly when heated, is partly hydrolysed with the production of an insoluble basic acetate or hydroxide, some of which remains in suspension. The suspended hydroxide wanders to the cathode during electrolysis, and acts as a protective colloid to the particles of copper electro-deposited, which are thereby prevented from becoming crystalline, so that the metal remains in the form of a solid gel. The presence of a protective colloid in copper acetate solution is demonstrated by the formation of an emulsion on shaking it with benzene, although the effect is less marked than with ferric acetate. All the properties of Schützenberger's copper, including its dissolution in ammonia

with evolution of nitrous oxide, can be explained on the colloid hypothesis.

The electrolysis between  $50^{\circ}$  and  $90^{\circ}$  of solutions of copper propionate, acetate, and formate in presence of gelatin gives rise to a series of golden to red cathode films. Some of the red films which were lacquered kept their colour for at least twelve months. Electrolysis below  $35^{\circ}$  gives rise to a pale brown deposit, which weighs 20 to 30% more than Faraday's law requires, and is contaminated with gelatin, copper oxide, and acetic acid or copper acetate. On immersion in one of the above electrolytes, it undergoes a remarkable series of colour changes to golden-brown, reddish-purple, purple, blue, light blue, olive-green. The blue patina is exceedingly beautiful, but unfortunately turns to a pale bluish-grey or olive-green on long exposure, and no means of fixing it could be found.

The production of these colours is analogous to photographic development. Dilute copper sulphate is to some extent active as a developer, and the formate more so, but the full blue colour was only obtained with the acetate and propionate. Other salts of copper are inactive. No appreciable change in weight occurs on development, but the blue colour is only on the surface of the film, which presents the ordinary copper colour at the back when stripped off the copper, brass, or platinum cathode. The blue is temporarily destroyed by hydrazine and by oxidising agents. No colour is developed on an oxidised film, but this can be sensitised again by reduction with hydrazine.

No good colour effects were obtained with films deposited in presence of colloids other than gelatin, but starch in acid solutions is slightly active, since it tends to accumulate at the cathode. The cathode deposits obtained from other salts of copper in presence of gelatin are abnormal, but none develop any colour in acetate solution.

It is supposed that the "development" of these cathode deposits consists in the adsorption of colloidal copper hydroxide from the solution by the deposit of colloidal copper. R. J. C.

Micrographic Notes on Copper. H. BAUCKE (*Intern. Zeitsch. Metallphysik*, 1913, 4, 155-166). Cold-worked copper undergoes recrystallisation at  $200^{\circ}$ , at which temperature the size of the crystal grains is a minimum. It increases very slowly up to  $700^{\circ}$ , and then very rapidly. Prolonged heating at  $450^{\circ}$  produces the same coarse structure as rapid heating to higher temperatures. Recrystallisation is also well marked after six hundred days at  $100^{\circ}$ . Superficial conversion of the hardened into annealed material at  $100^{\circ}$  is greatly accelerated by close contact with an etched, crystalline surface of copper. Prolonged etching with a dilute electrolyte also brings about conversion to the crystalline condition.

The oxide eutectic in copper undergoes segregation at  $800^{\circ}$  or upwards, but at  $450^{\circ}$  the effect is imperceptible after thirty days.

C. H. D.

**The Rare Earths. Yttrium Chloride and the Atomic Weight of Yttrium.** JAMES E. EGAN and CLARENCE W. BALKE (*J. Amer. Chem. Soc.*, 1913, **35**, 365-377).—Rare earths obtained from gadolinite and xenotime have been fractionated by various methods. Fractions obtained by James' bromate method (A., 1908, ii, 196, 499) have been submitted to Muthmann and Böhm's chromate method (A., 1900, ii, 209). It has been found that by this means small quantities of fairly pure yttria can be rapidly prepared from mixtures containing small amounts of erbium and holmium, but that the method cannot be applied to the fractionation of mixtures containing didymium and gadolinium, unless these are first removed by means of potassium sulphate.

The determination of the ratio  $\text{Yr}_2\text{O}_3 : \text{Yr}_2(\text{SO}_4)_3$  yielded values for the atomic weight which are lower than those obtained by other methods, but a study of the ratio  $\text{Yr}_2\text{O}_3 : 2\text{YrCl}_3$  gave values varying from 90.10 to 90.14 (O=16; Cl=35.16). Yttrium material containing not more than 0.5% of erbium, gave the value 90.12.

E. G.

**Yttrium Sodium Sulphate.** CHARLES JAMES and H. C. HOLLEY (*J. Amer. Chem. Soc.*, 1913, **35**, 559-563).—In using sodium sulphate for effecting the separation of the cerium and yttrium earths, varying results were obtained, and this has led to an investigation of the system, yttrium sulphate, sodium sulphate, and water. The results have shown that at 25° only one yttrium sodium sulphate exists, namely,  $\text{Yr}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , which has been described by Cleve. The solutions showed a tendency to remain in a metastable condition for many months. The efficiency of sodium sulphate for separating cerium and yttrium earths depends on its concentration; if the solution is too concentrated, much of the yttrium earths is precipitated.

E. G.

**Physico-chemical Researches on the Electrometallurgy of Aluminium.** PAUL PASCAL and ALCEGE JOUHANX (*Bull. Soc. Chim.*, 1913, [iv], **13**, 439-449).—Owing to the discordant and incomplete figures which are given in the literature on the thermal properties of mixtures of cryolite, alumina, and fluorspar, the subject has been systematically studied. About 35 grams of the pure substances were intimately mixed and pressed down in a nickel crucible, and then packed in a graphite crucible with iron filings and heated in the Meker furnace, the thermo-couple being used as a stirrer. Oxygen had the accepted m. p. 977°, but fluorspar was found to have m. p. 1361°, which is much higher than is usually stated. The eutectic mixture of cryolite and fluorspar had m. p. 905°, and was composed of 74.6% of the former, whilst the mixed crystals contained respectively 29.5% and 56% of the fluoride. The eutectic mixture of cryolite and alumina had m. p. 904°, and contained 24% of alumina, whilst the mixed crystals contained 20% and 29%. The mixture of fluorspar and alumina (26.5%) had m. p. 1270°, and gave crystals containing 20% and 28.5% of alumina.

In order to simplify the study of the ternary system the mixture

were arranged so that two of the constituents were in a proportion studied in the case of the binary mixtures. By triangulation the eutectic point was found to be 86% fluorite, 14% the mixture containing 59.3% cryolite, 23.0% fluorspar, and 17.7% alumina. The interpretation of the results was facilitated by the examination of the solidified mass. Mixtures which came within the cryolite section of the triangle presented a sugar-like fracture, those in the fluorspar section showed large cleavage faces with chatoyant reflexion, whilst the mixed crystals isomorphous with alumina were flattened, chiefly hexagonal, and had a grey reflexion.

Isotherms were also plotted. From them it is seen that this case is unusual, but rather ideal in that the maximum lowering of the melting point of a binary mixture is attained by adding the third constituent to the binary eutectic. Temperatures below 950°, which is the point aimed at in the manufacture of aluminium, are represented by a small quadrilateral, from which it is seen that the addition of more fluorspar than 36% of the cryolite must be avoided, whereas more alumina than is commonly used might be added, although the risk of volatilisation of cryolite makes it undesirable.

By measuring the temperature of final solidification it was possible to trace out the solidus with its thermic "bumping." This leads to the following compositions for the mixed crystals composing the ternary eutectic: - cryolite: fluorspar: alumina, I, 77: 16: 7; II, 60: 15: 25; III, 34: 54: 12.

J. C. W.

**The Formation of Aluminium Nitride from Alumina, Carbon, and Nitrogen.** 1. WALTER FRAENKEL (*Zeitsch. Elektrochem.*, 1913, **19**, 362-373).- The formation of aluminium nitride from alumina and nitrogen was studied with respect to the velocity of formation, temperature at which the reaction occurs, and the influence of the presence of carbon monoxide on the process. The reactions were effected in a carbon tube contained in a large glass vessel; the tube was electrically heated, and temperature readings were made by means of a Holborn-Karlbaum pyrometer. Alumina and carbon in the form of soot were mixed together in the proportion of  $2\text{Al}_2\text{O}_3 : 1\text{C}$ , and compressed into pellets of 0.5-1 gram. The reaction was carried out on one of the pellets in each case. It is shown that aluminium nitride is formed to a small extent below 1400°, and that at 1500° the velocity of formation becomes very great. The velocity is arrived at in the various experiments by allowing the reaction to proceed for a definite time (thirty minutes) and then boiling the product with alkali and estimating the ammonia evolved. The course of the reaction is expressed by the equation  $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ . This reaction is strongly endothermic, and proceeds at about the same rate when the pressure is reduced to 250 mm. of nitrogen. The presence of carbon monoxide diminishes the velocity of the reaction, and as this gas is a product of the reaction, experiments were made to see if the reaction was reversible. It is shown that at 1500° an equilibrium is set up when ca. a monoxide is present to 20-40 vol. %; at 1600° the

equilibrium occurs at 50—65 vol. % of carbon monoxide. When alumina is heated alone with carbon in carbon monoxide at 20—65 mm. pressure, reduction occurs at temperatures as low as 1450°, with the formation of aluminium carbide. The experiments show that, qualitatively at least, the formation of carbide runs parallel with the formation of nitride, and it is suggested that the nitride is formed through the carbide. The use of different forms of carbon causes the reaction to occur at different velocities. The authors can find no evidence to support the equation of Peacock and du Pont (U.S.A. Pat. 1031581/82), which represents the reaction in the following way:  $Al_2O_3 + 6C + 3N_2 = Al_2C_3N_6 + 3CO$ .  
J. F. S.

**"Liquefaction" of Clay by Alkali.** JOHANNES K. NEUBER (*Koll. Chem. Beshefte*, 1913, 4, 261—312).—The author has made a detailed investigation of the influence of sodium and calcium hydroxides on the thinning of clay pastes, both in the presence and absence of humus substances. With this object measurements have been made of the adsorption of the alkali by the clay, and also of the electrical conductivity and viscosity of clay suspensions containing alkali hydroxide in varying concentrations.

The results obtained in the investigation of the distribution of the alkali between water and the various clays indicate that the hydroxide is adsorbed in accordance with the ordinary exponential formula. This phenomenon is modified to a greater or less extent in the presence of humus substances, which combine with the alkali to form humates. The thinning of a clay mash in presence of alkali is to a large extent determined by the swelling of the humus substance in the clay particles; this leads to a process of disintegration, whereby larger quantities of alkali humate are formed, and this substance appears to play the part of a protective colloid.

On account of the chemical reaction which thus occurs in presence of humus, the distribution of the alkali between the solid and liquid phases is found to deviate very considerably from the requirements of the exponential formula when the concentration of the alkali hydroxide is very small.

The viscosity measurements indicate that slow changes occur in the character of the clay suspensions, but it seems probable that these can be accounted for on the basis of the swelling and disintegration processes referred to above.  
H. M. D.

**New Process for the Utilisation of Iron and Manganese Ores Rich in Silicon.** NAZARENO TARUGI (*Chem. Zeit.*, 1913, 37, 511—512).—In Italy and other countries there are considerable deposits of iron and manganese ores containing more than 20% of silicon, and the author proposes the following method for their utilisation. By the action of superheated steam on the ores, silicon chloride, hydrochloric acid is produced, with which the ores are then treated in suitable vessels. The chlorides of iron and manganese thus produced are separated from the silicon compounds by filtration, and the solution so obtained treated with the magnesium salt.

from the first process, whereby all the iron is precipitated as hydrated oxide and magnesium chloride regenerated.

The manganese can be separated from the iron by replacing part or all of the magnesium oxide by lime. The calcium chloride thus obtained can be converted into magnesium chloride by the addition of the requisite quantity of magnesia and treatment with carbon dioxide.

The products obtained are free from sulphur and phosphorus, no matter how much of these elements was present in the original ores.

T. S. P.

**The So-called Fibrous Structure in Mild Steel.** PAUL OBERHOFFER (*Zeitsch. anorg. Chem.*, 1913, **81**, 156—163).—A fibrous structure, due to parallel arrangement of ferrite and pearlite masses, presents itself in all hot-rolled steels, with the exception of pure pearlitic steel. All kinds of hot-working produce the effect, but its degree is dependent on the nature of the working, the temperature, and the rate of heating and cooling. The production of the structure is due to the influence of slag enclosures, which serve as nuclei for the recrystallisation of the ferrite. That part of the steel which is derived from the outside layer of the ingot, and is almost free from slag, does not develop the fibrous structure. The relation between structure and mechanical properties has also been determined.

C. H. D.

**The Toughness of Iron [Steel] at Different Temperatures.** PAUL GOERENS and G. HARTL (*Zeitsch. anorg. Chem.*, 1913, **81**, 130—141).—Tests have been made by heating or cooling the specimen beyond the required temperature, placing the bar on the anvil of the testing machine, and starting the test when a thermocouple indicates that the correct temperature has been reached. Charpy's method of shock-testing with notched bars has been used. The two steels contained 0.089 and 0.085% of carbon respectively, but specimens from the heads of the ingots, exhibiting considerable segregation, have also been examined.

The tests extend from  $-75^{\circ}$  to  $1000^{\circ}$ , and the curves of work done are very regular, showing distinct maxima at  $35^{\circ}$  and  $600^{\circ}$ , and a minimum at  $450^{\circ}$ . Above  $600^{\circ}$  the work done in fracture falls off rapidly. At  $-75^{\circ}$  the steel is brittle. Discontinuities at the critical temperatures of the steel are not observed. The curve showing the angle through which the bars are bent has a sharp minimum between  $450^{\circ}$  and  $500^{\circ}$ .

C. H. D.

**Action of Electrolytes on Metals under Stress.** H. RAVERT (*Intern. Zeitsch. Metallographie*, 1913, **4**, 129—142).—Steel balls used for bearings, when sawn through for microscopical examination and etched with hydrochloric acid (1:2), develop numerous cracks, the surface of the metal becoming first corrugated, after which rupture occurs. The effect is due to the action of the electrolyte in accelerating the passage from the metastable to the stable condition. Flaws in steel boiler-plates, in the neighbourhood of rivet-holes, where

the metal is locally strained, are also caused to spread by the action of acids.

C. H. D.

**The Transformations of Alloys of Iron and Silicon.** GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1913, **156**, 1240—1243).—A study of the dilatation curves of soft steels, containing varying percentages of silicon, shows that the addition of silicon has no appreciable effect on the dilatation between 0° and 700°. The irregularity in the dilatation curve for ordinary steel observed between 800° and 900° is not displaced on the temperature scale, but the departure from the regular curve becomes less, and finally vanishes with increase of silicon up to 1.3%. Thus with steels containing more than 1.3% of silicon the dilatation curve shows no transformation between 0° and 900°, whereas the cooling curve shows one at 700°.

W. G.

**The Transformation of Alloys of Iron and Silicon.** ÉMILE VIGOUROUX (*Compt. rend.*, 1913, **156**, 1374—1376).—A reply to Charpy and Cornu (preceding abstract), in which the author maintains that it is the point  $A_2$  which is of primary importance either in iron alone or alloyed with silicon, that the point  $A_3$  does not exist, and that the point  $A_1$  only occurs when carbon is present. In the re-heating of iron the transformation  $A_2$  begins at 726° and ends at 746°, the addition of silicon causing an immediate rise in this transformation temperature.

W. G.

**Influence of Manganese on the Mechanical and Structural Properties of Low Carbon Steels of Commercial Quality.** A. STADELER (*Ztsch. anorg. Chem.*, 1913, **81**, 61—69). Compare Lang, A., 1911, ii, 266).—Experiments with low-carbon steels, containing only 0.008% Si, and low phosphorus and sulphur, show that the tenacity is increased proportionately to the manganese up to 0.7% Mn. The elongation and contraction are not altered by manganese within that limit, and depend only on the carbon content. The presence of manganese is without influence on the microscopic structure.

C. H. D.

**Reciprocal Behaviour of Alkali Sulphates, Chromates, Molybdates, and Tungstates at Low and at High Temperatures.** II. MARIO AMADORI (*Atti R. Accad. Lincei*, 1913, iv, 22, 153—159). Compare A., 1912, ii, 557. The paper records the results of the thermal analysis of the systems:

$K_2SO_4$ ,  $K_2CrO_4$ ,  $K_2CrO_7$ ,  $K_2MoO_4$ , and  $K_2SO_4$ - $K_2MoO_4$ .

The m. p.s. of certain salts were found to be as follows: potassium sulphate, 1070°; potassium chromate, 978°; potassium molybdate, 926°; potassium tungstate, 894°. The transition points of these salts are: potassium sulphate, 585°; potassium chromate, 651°; potassium molybdate, 475°; potassium tungstate, 575°. The points obtained in the system  $K_2SO_4$ - $K_2CrO_4$  agree with those of Grossard (A., 1908, ii, 591). In the system  $K_2CrO_4$ - $K_2MoO_4$  the curve of crystallisation is also intermediate between the solidification tem-

peratures of the two salts. Mixtures up to 30 mol. % of chromate crystallise at the m. p. of the molybdate. The curve of the system  $K_2SO_4$ - $K_2MoO_4$  is also continuous, but there is a very flat minimum  $6^\circ$  below the m. p. of the molybdate. The m. p. of the mixture containing 45 mol. % of sulphate is equal to that of the pure molybdate. Analogous curves were obtained for the corresponding sodium salts by Boeke (*A.*, 1906, ii, 750). R. V. S.

**Electrochemistry of the Chromium Group. I. Tungsten and Uranium.** ARTHUR FISCHER (*Zeitsch. anorg. Chem.*, 1913, 81, 170-208).—[With A. RÖDERBERG.] Rods of metallic tungsten are prepared by Wartenberg's method (*A.*, 1907, ii, 697), using a modified apparatus with a cathode composed of tungsten impregnated with calcium and barium oxides, and an auxiliary tungsten electrode for starting the arc. The electrolyte used is an alcoholic solution of tungsten hexachloride, and the comparison electrode a calomel electrode in contact with an alcoholic solution of lithium chloride. Comparative measurements are made with alcoholic cupric chloride against the same electrode. Tungsten is found to occupy a place in the potential series between antimony and mercury. Passivity is not observed. The normal potential is at least 0.669 volt.

[With ERIC K. RIDEAL.]—It is not possible to obtain rods of uranium of sufficiently high conductivity for fusion by Wartenberg's method, and the material used for potential measurements is that obtained from oxide and carbon, fused in a vacuum furnace. It thus contains carbide. Using an alcoholic solution of uranium hexachloride, uranium is found to have a potential between copper and hydrogen.

It has not been found possible to obtain metallic tungsten by the electrolysis of alcoholic solutions of tungsten salts, or of an aqueous solution of pertungstic acid. Alcoholic tungsten hexachloride yields, in the cathode compartment, green crystals of the compound  $WCl_6(OEt)_3$  (this vol., i, 584). Uranium does not yield a similar product.

The electrolysis of solutions of uranium acetate yields a deposit of a hydrated uranium oxide. The conditions of deposition in different electrolytes have been determined. Both acid and alkaline solutions yield the uranium in the same state of oxidation.

#### C. II. D.

**Preparation of Pure Uranium.** A. RÖDERBERG (*Zeitsch. anorg. Chem.*, 1913, 81, 122-129).—Uranium has not yet been obtained in a sufficiently pure condition for measurements of the electrolytic potential. Uranium tetrachloride is best prepared by grinding the oxide,  $U_3O_8$ , with sugar and heating to redness, and then heating the product in a porcelain boat in a current of chlorine. The product always contains aluminium and silicon derived from the porcelain. When reduced by sodium in a closed iron vessel, much iron is always taken up. Nickel, magnesia, graphite, or silver vessel, are rapidly destroyed. Nickel steel is more resistant than iron or other steels.



The attempt has been made to reduce uranium tetrafluoride, which is more readily obtained pure. Sodium is not available for this purpose, on account of the sparing solubility of sodium fluoride in water, whilst potassium has been found to escape in the form of vapour, even when the joints of the vessel are tightly made.

C. H. D.

**The Equilibrium Tetragonal Tin - Rhombic Tin.** ERNST CONIX (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 839-840).—Polémique against Smits and de Leeuw (this vol., ii, 141).

H. M. D.

**Oxidation of Stannous Chloride in the Air in Presence of Ferrous Chloride.** T. WARYŃSKI and W. TOWKIEWICZ (*Ann. Chim. anal.*, 1913, 18, 130-132).—Of twenty-five salts experimented with, the only one that strongly accelerates the oxidation of stannous chloride dissolved in dilute hydrochloric acid is ferrous chloride. From the tables given, it is evident that the maximum effect is obtained when 1 mol. of ferrous chloride is added to 100 mols. of stannous chloride. If more is added, the action decreases.

L. DE K.

**Compounds of Titanium Dioxide with Selenic and Selenious Acids.** HANS BRENER (*Zeitsch. anorg. Chem.*, 1913, 80, 148-152).—A solution of  $\alpha$ -titanic acid in hot dilute sulphuric acid is boiled with selenic acid. The white precipitate has the composition  $\text{TiO}_2 \cdot \text{SeO}_3 \cdot \text{H}_2\text{O}$ , whilst with one-half the quantity of selenic acid a similar compound,  $2\text{TiO}_2 \cdot \text{SeO}_3 \cdot \text{H}_2\text{O}$ , is obtained. Selenious acid also yields two compounds,  $\text{TiO}_2 \cdot \text{SeO}_2 \cdot \text{H}_2\text{O}$  and  $2\text{TiO}_2 \cdot \text{SeO}_2 \cdot \text{H}_2\text{O}$ . The selenious compounds dissolve more readily in water than the selenic compounds. All are soluble in hot mineral acids.

C. H. D.

**Zirconium Carbonates.** EDOUARD CHAUVENET (*Bull. Soc. chim.*, 1913, [iv], 13, 454-457).—Dry zirconium oxide does not combine directly with carbon dioxide, but at temperatures below 450° it absorbs a small amount of the gas. When a zirconium salt is precipitated by sodium carbonate of any concentration, the hydrate,  $\text{ZrCO}_3 \cdot \text{ZrO}_2 \cdot 3\text{H}_2\text{O}$ , is precipitated as a gelatinous, microcrystalline mass (compare Berzelius, *Ann. Chim. Phys.*, 1825, 337; Hermann, *Jahresb.*, 1856, 89, 191), which changes into the hydrate with  $2\text{H}_2\text{O}$  in an exhausted desiccator. Above 60° it begins to lose carbon dioxide as well as water, and forms  $2\text{ZrCO}_3 \cdot 3\text{ZrO}_2 \cdot 3\text{H}_2\text{O}$ , which towards 250° becomes still more basic and agrees with  $\text{ZrCO}_3 \cdot 3\text{ZrO}_2 \cdot \text{H}_2\text{O}$ , and then steadily decomposes, until at 400° pure oxide remains. An anhydrous carbonate seems incapable of existence. Like thorium, zirconium forms ortho-carbonates, but unlike that metal, it only yields a basic carbonate by precipitation. Under 20 or 30 atmospheres pressure, however, the dihydrated basic carbonate absorbs carbon dioxide, and forms a hydrated normal carbonate,  $\text{CO}_2 \cdot \text{Zr} \cdot 2\text{H}_2\text{O}$ .

J. C. W.

**Chemistry of Gold.** VICTOR LEBNER (*J. Amer. Chem. Soc.*, 1913, 35, 546-552).—An examination of the action of various reagents

reducing agents on auric chloride has shown that aurous compounds cannot be obtained in this way. In alkaline solutions, numerous compounds, such as formic and lactic acids, formaldehyde, acetone, phenol, and aniline, cause the immediate precipitation of gold, whilst a few substances, such as pyrogallol, quinol, and other photographic developers, produce the same effect in acid solutions. Many organic liquids which are immiscible with water extract auric chloride from its aqueous solutions.

Of inorganic reducing agents, sulphurous acid and arsenious oxide are capable of reducing auric salts to the aurous state, but all other reagents studied cause the precipitation of gold. Sulphurous acid has proved the most satisfactory for the purpose (compare Diemer, following abstract). E. G.

**Aurous Chloride.** MELVIS E. DIEMER (*J. Amer. Chem. Soc.*, 1913, 35, 552—559).—When auric chloride, containing hydrochloric acid and water, is heated at 100°, it gradually loses weight, and is converted into the metal. If, however, the auric chloride is prepared by dissolving gold in aqua regia, evaporating the solution, and heating the residue at 200° in a current of chlorine, it is obtained free from hydrogen chloride and water. When such anhydrous auric chloride is heated at 190° and weighed at regular intervals, it is found that at a certain point it is completely converted into aurous chloride. Aurous chloride is rapidly decomposed by water in accordance with the equation  $3\text{AuCl} = 2\text{Au} + \text{AuCl}_3$ . When a solution of the salt in ammonia is acidified with hydrochloric acid, the compound,  $\text{AuNH}_2\text{Cl}$ , is obtained as a white, crystalline precipitate, and is very unstable.

When a solution of auric chloride is treated with sulphur dioxide, its colour is reduced to some extent, but, before it becomes colourless, decomposition takes place, and gold separates. If chloride of sodium, potassium, ammonium, calcium, or magnesium is added to an auric chloride solution, the yellow colour can be entirely removed by sulphur dioxide, and this reaction can be used for the volumetric estimation of gold. Determinations have been made of the single potential of gold in an auric chloride solution at various stages of its reduction by sulphur dioxide in presence of each of the chlorides mentioned, and all the curves obtained show a decided break corresponding with the formation of an aurous compound at an intermediate stage of the reduction. Further experiments have afforded evidence that in such solutions aurous chloride exists as a compound of the type  $\text{AuCl} \cdot \text{NaCl}$ , which is unstable except in presence of a large amount of the chloride of the alkali metal. When these double compounds suffer decomposition, the solution becomes yellow, owing to the formation of auric chloride, and gold is precipitated. E. G.

## Mineralogical Chemistry.

**The Melting Points of Some of the Rarer Minerals.** ARNOLD L. FLETCHER (*Sci. Proc. Roy. Dubl. Soc.*, 1913, 13, 443—459).—The melting points were obtained with an improved form of the Joly melfometer, in which the temperatures were determined by measuring the extension of the platinum strip on heating. The instrument was calibrated with substances of known melting point, and could be used for temperatures between  $300^{\circ}$  and about  $1600^{\circ}$ .

The melting points and behaviour of minerals belonging to the following classes were investigated: fluorides, orthosilicates, subsilicates, titanosilicates, columbates and tantalates, phosphates and arsenates, and uranates.

The results obtained by Cusack (*A.*, 1898, ii, 383) are corrected in the light of the author's results. T. S. P.

**Maucherite, a New Nickel Mineral from Thuringia** FRIEDRICH GRUNLING (*Centr. Min.*, 1913, 225—226).—This new mineral, which was at first mistaken for rammeisbergite, occurs together with niccolite, chloanthite, native bismuth, calcite, barites, manganite, etc., in veins (Kobaltrücken) in the copper-shale (Kupferschiefer) at Eisleben, Thuringia. The crystals have the form of rectangular plates (tetragonal or orthorhombic), and are arranged in fan-shaped groups; compact, fibrous, and cellular masses also occur. The colour is reddish-silver-white, altering to greyish-copper-red, and the streak blackish-grey. D 7.83. Analyses, I by Friedrich, and II by Prandl, give the formula  $\text{Ni}_2\text{As}_2$ .

	As.	S.	Ni.	Co.	Pb.	Fe.	Anal.	Total.
I.	45.96	—	19.51	0.26	—	—	—	65.73
II.	47.67	0.17	32.73	2.15	0.20	0.40	0.40	83.72

L. J. S.

**The Natural Crystalline Carbonates of Calcium, Magnesium, Iron, and Manganese.** KARL GRUNBERG (*Zeitsch. anorg. Chem.*, 1913, 80, 337—396).—The material employed in this investigation includes ankerites, in which the molecular proportion of calcium carbonates is equal to the sum of the carbonates of magnesium, iron, and manganese; dolomitic rocks, in which the proportion of calcium is lower; and chalybeates, containing the carbonates of iron, manganese, and magnesium, with little or no calcium. Determinations of density show that the density of ankerites varies in a linear manner between the limits  $\text{CaFe}(\text{CO}_3)_2$  and  $\text{CaMg}(\text{CO}_3)_2$ , whilst the former compound has a density which is the mean of those calculated from calcite and siderite.

By heating the powdered minerals in a silica vessel in a stream of hot air, free from carbon dioxide, the rate of dissociation of the carbonates has been determined. When a mixture of artificial

magnesite, dolomite, and calcite is thus heated, the magnesite is first completely decomposed at  $419^{\circ}$ ; the dolomite loses carbon dioxide corresponding with its magnesium content at  $500^{\circ}$  and with its calcium content at  $539^{\circ}$ ; finally the calcite is decomposed at  $570^{\circ}$ . The same order is observed when a stream of carbon dioxide is used. Determinations with ankerite and two dolomitic rocks indicate that in both materials there is no compound of magnesium and calcium carbonates, but that mixtures of ankerite with calcite are present. On the other hand, another dolomitic rock behaves as a mixture of dolomite and magnesite. Microchemical methods of distinguishing the intermixed carbonates in thin sections are described.

Dilute hydrochloric acid attacks chalybite much more slowly than ankerite, and the solution always contains relatively more iron and less manganese than the original mineral. The compound  $\text{CaFe}(\text{CO}_3)_2$  is more readily attacked than  $\text{CaMn}(\text{CO}_3)_2$ , with which it is isomorphous, whilst the third component of ankerite, the compound  $\text{CaMn}(\text{CO}_3)_2$ , is the most resistant of all. Ankerite and dolomite are decomposed as such, and not fractionally. Similar conclusions are drawn from the action of copper nitrate on the minerals, but the differences of solubility are even greater than with hydrochloric acid. C. H. D.

**Certain Sulphates from the Neighbourhood of the Monastery of St. George in the Crimea.** SERGEI I. POROV (*Bull. Acad. Sci. St. Petersburg*, 1913, 253—256). Pebbles on the shores of the Black Sea, near the Monastery of St. George, are coated with white and yellow mineral deposits, which are found to be sulphates of various compositions. One of the purest of these, which was white with a very faint bluish-green tint, gave the following percentage results on analysis:

	Invol.									
	$\text{SO}_3$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{NiO}$	$\text{H}_2\text{O}$	Total
	36.25	11.42	trace	1.98	9.42	38	6.33	9.19	45.78	97.1
										100.00

If the  $\text{CaO}$ ,  $\text{NiO}$ ,  $\text{MnO}$ , and  $\text{Na}_2\text{O}$  are calculated as  $\text{MgO}$ , the above figures correspond well with the formula  $\text{MgAl}_2(\text{SO}_4)_6 \cdot 22\text{H}_2\text{O}$ , which is that of pickeringite. Partial replacement of the magnesium by other oxides has been observed in other samples of pickeringite. In other specimens of the white sulphate, the ratio between the oxides  $\text{R}_2\text{O}_3$  and  $\text{RO}$  was found to be different from that shown above.

The yellow substances consist of iron sulphates containing free sulphur and various impurities. Gypsum is also found.

The formation of pickeringite and other aluminosulphates is regarded as due to the action on the aluminosilicates of the pebbles of sulphuric acid resulting from the weathering of pyrites; the latter may also be the source of the copper and nickel. T. H. P.

**Attempts to Produce Mixed Crystals of Diopside and Jadeite.** VERA SCHUMOFF-DELEANO (*Centr. Min.*, 1913, 227—230).—Mixtures of artificial diopside ( $\text{CaMgSi}_2\text{O}_6$ ) and jadeite ( $\text{NaAlSi}_2\text{O}_6$ )

were fused, and the products examined microscopically. A homogeneous, crystalline mass is obtained only when less than 5% of jadeite is present. The optical characters ( $\gamma = 39^\circ$ ,  $n_\gamma = 1.689$ ) are practically the same as those for pure diopside; *m. p.* 1150–1200° (that of pure diopside being 1260–1300°). With more jadeite in the mixture, the product contains crystals of two kinds and some glass; and with still richer mixtures, only glass. Jadeite could not be crystallised artificially.

Diopside, when fused with sodium aluminate,  $\text{NaAlO}_2$ , takes up some alumina, with a slight increase in the angle of optical extinction. I. J. S.

**Chemical Constitution of Nephelite.** V. V. KARANDÉV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 267–277).—The author describes a specimen of ecloelite from Mias, near the shores of Lake Ilmen. The mineral, which has a pale rose colour and a fatty lustre, has  $D_{20}^{25-27}$  2.6296, and gives the following results on analysis:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	Loss on heating	Total
63.61	33.84	0.41	19.11	5.82	0.84	100.63

These figures are discussed in relation to the various views which have been expressed concerning the chemical structure of nephelite (compare Thugutt, A., 1895, ii, 358; Rammelsberg, A., 1896, ii, 189; Clarke, A., 1897, ii, 51; Morozewicz, A., 1908, ii, 201; Wallae, A., 1909, ii, 665; Foote and Bradley, A., 1911, ii, 122; Bowen, A., 1912, ii, 176, 771). T. H. P.

**Chemical Investigation of Certain Minerals from Ceylon Gravel.** II. GEORGE P. TSCHERNIS (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 365–376). Compare this vol., ii, 421).—The gravel from the Sabaragamuwa province of Ceylon contains a mineral which occurs in the form of dull, greyish-black pebbles,  $D_{20}^{25}$  4.68, with a velvety-black, flat conchoidal, glassy fracture. It shows neither cleavage nor crystalline form, and exhibits but slight transparency, thin chips transmitting yellowish-brown light at their edges. It gives a dark brown streak, and scratches apatite, but not orthoclase. Its percentage composition is as follows:

$\text{SiO}_2$	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Y}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{FeO}$	$\text{ZrO}_2$	$\text{FeO}$	$\text{MnO}$
24.73	19.55	22.25	1.56	0.78	3.27	2.61	5.12	0.97
		$\text{CaO}$	$\text{MgO}$	$\text{BaO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{H}_2\text{O}$	$\text{F}_2\text{O}$
		0.91	0.22	0.91	1.05	trace	2.50	

These results are expressed by the formula  $60\text{FeO} \cdot 28\text{SiO}_2 \cdot 2\text{Fe}_2\text{O}_3(\text{SiO}_2)_3 + 6\text{FeO}(\text{TiO}_2) + 3\text{FeO}(\text{FeO}) + 2\text{ZrO}(\text{TiO}_2)$ , which, together with the physical properties, indicate that the mineral belongs to the tscheffkinites. T. H. P.

**Application of Colloidal Chemistry to Mineralogy and Geology.** Nature of Moerschau. II. MÜLLER (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 165–170).—An examination has been made

of the microscopic structure, the optical properties, and the behaviour towards dyes of different samples of meerschaum obtained from various sources. The observations seem to show that the meerschaums consist of mixtures of a fibrous, crystalline silicate with constant optical properties, and of a gel. The crystalline constituent is basic and absorbs acid dyes, whilst the isotropic substance is acidic and absorbs basic dyes. When a finely powdered sample of meerschaum is subjected to the action of a solution containing methylene-blue and magenta, it is found that the mineral becomes blue and the solution red. This is attributed to the much greater rate at which the basic dye is absorbed by the gel. The variable water content of the meerschaums is probably connected with the varying proportion of the two constituents, for the constancy of the optical properties of the crystalline constituent would seem to show that the proportion of water in this is quite constant.

H. M. D.

**Behaviour of Cimolite before the Blowpipe with Cobalt Solution.** HERMANN STRENKE (*Centr. Min.*, 1913, 313-318).—A farther criticism and reply to Thngutt (A., 1912, ii, 267) on the constitution of the minerals of the allophane group. The cimolite from Bilin, Bohemia, examined by Thngutt, does not become blue when ignited with cobalt solution, and he consequently drew the conclusion that this mineral represents a definite compound of alumina, silica, and water. His analysis showed, however, 2.49% FeO, and this is sufficient to mask any coloration. L. J. S.

**Cancrinite- and Nephelite-bearing Bombs from the Laacher See District.** REINHARD BRAUNS and JOHANNES UHLIG (*Jahrb. Min.*, 1913, *Beil.-Bd.*, 35, 119-220, 723-752).—The first part, by R. Brauns, gives a detailed petrographical description of these ejected volcanic-blocks, with an account of their contained minerals; and the second part, by J. Uhlig, gives an account of the chemical examination of the materials. Details are given of the methods of analysis, especially with regard to the detection of traces and the estimation of small amounts of the rare elements (tantalum, glucinum, etc.), the presence of which have not before been detected in these minerals. Analysis I of the nephelite gives the ratio  $\text{SiO}_2 : \text{Al}_2\text{O}_3 : (\text{Na}, \text{K})_2\text{O} :: 2.25 : 1 : 1.02$  (compare Morozewicz, A., 1908, ii, 201). Analysis II of cancrinite agrees with the formula  $\text{Na}_{20}\text{Al}_{20}\text{Si}_{12}\text{O}_{48}\text{Ca}_4\text{Na}_2(\text{CO}_3)_5 \cdot 5\text{H}_2\text{O}$ . Analysis III of dayne gives  $\text{Na}_{20}\text{Al}_{20}\text{Si}_{22}\text{O}_{65}\text{Ca}_4\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ . A sodium-potassium feldspar (microperthite) gave IV. These analyses and formulae are discussed in detail; and bulk analyses of the rocks are also given.

	$\text{SiO}_2$	Ta <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	GdO	MnO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Cl	CO <sub>2</sub>	H <sub>2</sub> O	Total	Sp. 25
I.	51.70	trace	32.60	0.56	0.58	trace	0.52	17.50	4.97	0.06	—	—	100.0	2.0
II.	50.20	0.74	27.41	0.9	0.5	—	0.1	17.38	1.00	0.01	0.23	0.07	100.0	2.11
III.	53.65	0.11	27.07	0.57	0.10	0.14	0.75	2.64	8.00	0.09	0.28	0.05	100.0	2.51
IV.	60.10	trace	19.58	0.20	—	trace	0.08	8.90	0.48	—	—	0.04	100.0	—

Also TiO<sub>2</sub> trace, P<sub>2</sub>O<sub>5</sub> trace, Ce<sub>2</sub>O<sub>3</sub> trace, UO<sub>2</sub> trace, S<sub>2</sub> trace, MnO trace.  
Also Cl<sub>2</sub> trace, MgO trace.

L. J. S.

**Meteorite from near Cullison, Kansas.** GEORGE P. MERRILL (*Proc. U.S. Nat. Mus.*, 1913, **44**, 325—330).—This stone, weighing 10.10 kilos., was found in 1911 near Cullison, in Pratt Co., Kansas, and is stated to have fallen on December 22nd, 1902. On the broken surface it is black and very dense, showing no apparent structure, but on a polished surface it exhibits abundant metallic specks, numerous chondrules, a large, light-coloured patch, and an obscure banded structure suggestive of shearing. Under the microscope is seen a dense aggregate of small chondrules of various shapes; the recognisable minerals are olivine, orthorhombic and monoclinic pyroxenes, and fragmentary plagioclase feldspars, together with metallic iron and iron sulphide. D 3.65. Chemical and mechanical analyses by J. E. Whitfield yielded the following results. A separation by means of an electromagnet and treatment of the residue with iodine gave: iron sulphide (troilite or pyrrhotite), 6.00; metallic iron, 19.10; silicates, 74.50; schreibersite, 0.40. The metallic portion yielded I, and the silicate portion II, from which the bulk composition under III is calculated:

	Si	S	P	Ni	Co	Cu	Cr	C	Mn	Fe	$\frac{Mo, W, V}{100}$	Tot.
I.	0.129	0.135	0.071	0.297	0.507	0.010	0.160	0.088	0.06	89.700	0.000	90.000
II.	—	—	—	—	—	—	—	—	—	—	—	—
III.	—	2.184	0.011	1.89	0.098	0.008	0.029	0.017	0.015	21.279	—	—
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	FeO	CaO	MgO	MnO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	Tot.	
I.	47.36	5.67	0.10	11.25	0.84	31.79	0.36	2.32	0.23	0.00	100.00	
II.	55.30	4.21	0.75	8.38	0.02	23.61	0.268	1.801	0.171	—	100.00	

The powdered stone, when digested with distilled water, gave a trace of calcium, and with very dilute hydrochloric acid 0.25% Cu, 0.05% SO<sub>2</sub>, and 1.14% MgO (the last, no doubt, derived from the olivine). These results suggest the presence of the mineral dolomite (CaMgSiO<sub>4</sub>) or of its weathered representative gypsum. L. J. S.

**The Minor Constituents of Meteorites.** GEORGE P. MERRILL (*Amer. J. Sci.*, 1913, [iv] **35**, 509—525). The elements well known to be present in meteorites are silicon, aluminium, iron, chromium, manganese, nickel, cobalt, magnesium, calcium, sodium, potassium, sulphur, phosphorus, and carbon. In addition to these, the following have been reported, some of which are doubtful (a summary of the literature is given): arsenic, antimony, copper, gold, lead, bismuth, palladium, platinum, iridium, tin, titanium, tungsten, uranium, vanadium, and zinc. Samples of not less than 50 grams of each of the following eleven meteorites have been specially examined by J. E. Whitfield for the presence of these rarer elements. The accidental presence of platinum is confirmed, and of vanadium in two instances; palladium and ruthenium were found in one sample. I. Iron from Canyon Diablo, Arizona; anal. I, also, FeO, 96.76. II. Iron from Casas Grandes, Mexico. III. Iron from Meteor Crater, Pennsylvania; Cr, 0.006; Mn, 0.075; Cu, 0.008; Cl, 0.275; Pt, trace. IV. Iron from Perryville, Missouri (this vol., ii, 121). V. Stony iron (pallasite) from Mt. Vernon, Kentucky; also, Cr, 0.265; V, trace.

	Si.	S.	P.	Mn.	Cu.	Ni.	Co.	C. (0.01 bind.)	C. (0.0100 bind.)	Fe.	Total.
I.	trace	0.009	0.261	nil	0.015	7.335	0.510	0.105	0.928	2.520	89.167
II.	0.010	0.020	0.106	—	0.012	7.742	0.601	0.145	0.932	9.791	169.017
V.	—	—	—	0.151	0.016	2.360	0.690	—	—	—	—

VI, Stone from Selma, Alabama; also,  $V_2O_5$  trace. VII, Stone from Ness County, Kansas; also, loss on ignition 3.50, Fe 13.86, Ni 1.05, Co 0.03, Cu 0.05. VIII, Stone from Cullison, Kansas (see preceding abstract). IX, Stone from MacKinney, Collin Co. Texas, consisting of troilite (FeS) 6.26, schreibersite 0.58, metal 5.70, chromite 0.11, silicates 87.35; the silicate portion gave anal. IX, and the metallic portion contained Ni 13.16, Co 0.92, Cu 0.08, Fe [85.84]=100.00. X, Stone from Holbrook, Arizona (this vol., ii, 71). XI, Stony iron (pallasite) from Krasnojarsk, Siberia, specially examined for arsenic and tin, but no trace of these detected. Comparisons are made between the chemical composition of these meteorites and of the ultra-basic terrestrial rocks.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	MnO	NiO	CuO	Total.
VI.	32.40	4.88	37.09	6.10	1.52	21.66	9.27	1.88	99.31
VII.	38.34	8.259	8.551	9.57	1.18	24.61	—	—	80.447
IX.	43.30	15.18	8.45*	—	1.88	30.48	6.25	0.51	100.05

\* FeO.

L. J. S.

### Analytical Chemistry.

**A Rennew Method of Obtaining Sublimates.** ARNOLD L. FLEISCHER (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **13**, 460—466).—The sublimation chamber is a cylindrical, wooden or porcelain box, 5—6 cm. in diameter and 3 cm. in height, with walls about 1 cm. in thickness. A pair of forceps is fitted internally on each side of the box, and connected through the walls with terminals for the source of current; they are hinged at a short distance from the internal face, and are of sufficient length to reach nearly to the top of the box when bent at right angles at the hinge. The forceps carry a carbon rod (in some cases a platinum strip is used), on which the substance to be heated is placed. The sublimation chamber is closed above and below by cover plates, and is fitted with inlet and outlet tubes, so that the heating process may be carried out in any desired atmosphere. The cover plates may consist of glass, clear or opaque silica, biscuit ware, plaster of Paris, or even white paper, and may be raised if necessary by circular washers. A glass cover plate is conveniently cooled by a drop of water on its upper surface.

With the above apparatus it is possible to examine the effect of heat on substances in different atmospheres, sublimates being formed



with the same facility in these atmospheres as they are in air. Mixtures or alloys, such as brass, or even steel, may be dealt with to a certain extent by fractional volatilisation, the deposits produced being removed on separate cover glasses. Very small quantities of impurities in metals can thus be detected, the cadmium present in commercial zinc being easily distinguishable.

This method of analysis possesses a range of action enormously superior to that of the blowpipe, and is limited only by the volatility of the carbon; only very small quantities of material are necessary.

The results of experiments with the various solid elements in the periodic system are given.

T. S. P.

**Removal of Fusions in Alkali Carbonates from the Crucible.** R. HOWDEN (*Chem. News*, 1913, 107, 232).—At the end of the fusion a pinch of powdered nitre is added to the still liquid mass. This causes the same to become more porous on cooling, owing to gases being evolved, and to be more readily disintegrated by water.

L. DE K.

**The Use of Extract of Red Cabbage as an Indicator for Colorimetric Estimation of the Hydrogen Ion Concentration.** L. E. WALBUM (*Biochem. Zeitsch.*, 1913, 50, 346. Compare this vol., ii, 237).—Reply to a claim for priority by E. Fuld.

S. B. S.

**Theory of Indicators.** JOHN WADDELL (*Chem. News*, 1913, 107, 206).—According to the ordinary theory of indicators, it is strange that methyl-orange, a strong acid, should act towards weak acids in exactly the same way as phenolphthalein, a weak acid, acts towards weak bases. This anomaly is removed if methyl-orange is considered to be a weak base, and not a strong acid, and the author gives experiments which indicate the basic behaviour of methyl-orange. According to the ordinary theory, the pink colour is due to the undissociated substance, and the yellow colour to the dissociated ion; all means of diminishing the dissociation, however, tend to change the colour from pink to yellow; for example, glacial acetic acid to which methyl-orange is added gives a red colour, which may be lessened, if not destroyed, by the addition of acetates, and is easily changed to yellow by the addition of alcohol. Other experiments are quoted, of a similar nature, indicating that the yellow colour of methyl-orange is that of the undissociated compound, the red being due to the dissociated cation (compare Noyes, *A.*, 1910, ii, 746).

T. S. P.

**The Development of Electro-analysis.** REMIGIUS FRIESEN (*Zeit.-ch. anorg. Chem.*, 1913, 81, 4–23).—An historical account of the introduction of electrolytic methods of analysis, with bibliographical references.

C. H. D.

**New Electrode for Electrolytic Analysis.** L. BERTHAUD (*Ann. Chim. anal.*, 1913, 18, 129–133).—A slight modification of the

Holland apparatus, so as to render it more stable. The electrode consists of a cylinder of perforated foil composed of an alloy of platinum with 10% of iridium, to which has been sealed a rigid stem of the same alloy. The spiral used with this electrode is about the same as that in Holland's apparatus, only is a little more cylindrical in form.

L. DE K.

**Estimation of Water in the Volatile Products Obtained in the Distillation of Fuels.** GUSTAV LAMBRIS (*Zeitsch. anorg. Chem.*, 1913, 81, 24--39).—Phosphoric oxide is the only drying agent available for the estimation of water in the products of distillation of fuels, as sulphuric acid or salts either combine with hydrocarbons and other impurities, or again give up the water at the temperature necessary to expel tarry products. The only impurities retained by phosphoric oxide are ammonia, pyridine bases, and phenol. These substances are retained quantitatively, and may be estimated by the following method. The phosphoric oxide must be free from lower oxides. After absorption and weighing, it is dissolved in water, made strongly alkaline, and distilled. The distillate is absorbed in a known quantity of sulphuric acid, and the excess of acid titrated with sodium hydroxide, using Congo-red as an indicator, and evaporated to dryness. The residue is heated to 130° to expel pyridine, and the sulphuric acid thus set free is titrated. Unless the ammonia present is largely in excess of the pyridine, it is necessary to add a known quantity of ammonium sulphate to the residue before heating; otherwise the expulsion of pyridine is incomplete. Pyridine bases are estimated in similar manner, but longer heating is required, and the result obtained must be multiplied by a corresponding factor. Phenol is estimated by the usual bromide-bromate method, metaphosphoric acid being without disturbing influence. These methods allow of a complete correction for impurities in the aqueous distillate.

C. H. D.

**Estimation of the Water Formed in the Combustion of Substances containing Sulphur and Nitrogen in the Calorimetric Bomb.** O. RAV (*Zeitsch. anorg. Chem.*, 1913, 81, 116-121).—The estimation of nitric and sulphuric acid is necessary in order to determine the proper correction of gross to net calorific values. The method recommended is that of mixing a small quantity of dry sodium carbonate with the fuel before combustion. After combustion, the bomb is immersed in an oil bath at 110°, and the gas allowed to escape slowly through a large absorption apparatus, a current of air, free from moisture and carbon dioxide, being then passed through. Water and carbon dioxide are thus estimated. The residue in the bomb is washed out with water, titrated with  $N/5$  hydrochloric acid and methyl-orange, warmed, and precipitated by means of  $N/5$  barium chloride. After the precipitate has settled,  $N/5$  sodium carbonate is added, the solution is cooled, diluted to a definite volume, filtered through a dry filter, and a measured quantity of the filtrate titrated with  $N/5$  hydrochloric acid. The nitric and sulphuric acids may thus be calculated. The

correction of the calorific value for water and acids amounts, in the case of coal, to about 1.5%, whereas the sodium peroxide method involves a correction of 30%.

The carbon dioxide estimated in this way is always about 1% low.

C. H. D.

**Estimation of Iodine in Syrup of Iodotannin.** M. EMMANUEL POZZI-ESCOR (*Bull. Soc. chim.*, 1913, [iv], 13, 403—404).—Twenty c.c. of the syrup, diluted with 50 c.c. of water, are placed in a "bromine tube" with 10 c.c. of chloroform, and then 2 c.c. of sulphuric acid and excess of a saturated solution of potassium permanganate added. The mixture is shaken to dissolve the iodine in the chloroform, and the latter is decanted and the extraction continued with two further portions of chloroform, each of 10 c.c. The united chloroform solutions are then titrated with sodium tetrathionate solution.

T. A. H.

**Estimation of Oxygen in Metallic Tungsten Powder and Some Notes on the Estimation of Oxygen in Steel.** CHARLES MORRIS JOHNSON (*J. Ind. Eng. Chem.*, 1913, 5, 295—297).—A detailed description is given of the method of estimating oxygen in tungsten powder, which involves heating the metal in a current of hydrogen. The hydrogen employed is passed through vessels containing potassium hydroxide solution, alkaline pyrogallol solution, calcium chloride, potassium hydroxide, and phosphoric oxide respectively, before it enters the quartz combustion tube, in which the metal is heated to a temperature of 950—1000° by means of an electric furnace. The metal is dried at 105° previous to the estimation, and the necessary precautions are taken to remove all air from the apparatus before the heating part of the process is commenced. The water produced is collected and weighed in a tube containing phosphoric oxide. The presence of excessive amounts of free carbon in tungsten oxide does not affect the results obtained, but low results are found in the case of ferric oxide when this contains more than 5% of free carbon. Attention is drawn to the fact that steel undergoes decarbonisation when heated in a current of hydrogen; for instance, a steel containing 1.08% of carbon was found to contain only 0.83% after having been heated for three and a-half hours in hydrogen.

W. P. S.

**Estimation of Ozone and Hydrogen Peroxide.** VICTOR ROTHMUND and A. BRUGSTALLER (*Monatsh.*, 1913, 34, 693—701).—Although molybdic acid catalyses the reaction between hydrogen peroxide and hydriodic acid (potassium iodide in acid solution), it does not catalyse the oxidation of hydriodic acid by dissolved oxygen or air (compare Lather and Inglis, A., 1903, ii, 406). It can consequently be used as a catalyst in the volumetric estimation of hydrogen peroxide in acid solution, accurate results being obtained.

Attempts to estimate a mixture of ozone and hydrogen peroxide by a direct method, using potassium iodide, were not successful.

The following indirect method gives good results. The slightly acid (0.01N) solution of ozone and hydrogen peroxide is added to excess of potassium bromide at 0°, whereby bromine is liberated by the ozone (compare Inglis, T., 1903, **83**, 1010; Treadwell and Anneler, A., 1906, ii, 123); an excess of potassium bromide is necessary in order to prevent further action between bromine and hydrogen peroxide. A slight excess of potassium iodide is then added, and the liberated iodine titrated, after which the solution is acidified with dilute sulphuric acid, and ammonium molybdate and more potassium iodide added. After five minutes, the liberated iodine is again titrated, this giving the amount of hydrogen peroxide present. T. S. P.

**Estimation of Sulphur Dioxide in the Air.** CARL KULLGREN (*Arkiv. Kem. Min. Geol.*, 1913, **4**, No. 31, 1—26).—While investigating the conductivities of very dilute solutions, the author made the observation that in certain cases the conductivity increased to some extent (about 1%) at the commencement of the experiments. Similar results were obtained when conductivity water was used. It was ultimately found that sulphur dioxide present in the air, especially in a room where gas was burning, was the cause of these anomalous results. During the drying of the electrodes the sulphur dioxide is absorbed by the platinum black and oxidised catalytically to sulphuric acid, which then dissolves in the solutions or water under investigation, and increases the conductivity. Carbon dioxide or ammonia does not have a similar effect.

On the above observations the author has based a method for estimating the amount of sulphur dioxide in the air. About 40 litres of the air are drawn through platinum black placed on a platinum sieve at the bottom of a tube of platinum, the time necessary being about 15 minutes. The tube and black are then immersed in water to dissolve out the sulphuric acid, and the conductivity of the solution measured. Preliminary experiments with known quantities of sulphur dioxide showed that the conductivity of the solution formed is directly proportional to the amount of sulphur dioxide when no allowance is made for the conductivity of the water used. T. S. P.

**Titration of Sulphurous Acid, also in Presence of Thio-sulphuric Acid.** EMIL BOSSHARD and W. GRON (*Chem. Zeit.*, 1913, **37**, 465—466).—*Sulphite—Acid Sulphite*.—Fifty c.c. of the solution (about 0.5 gram of solid salts) are titrated with N 5-hydrochloric acid, with methyl-orange as indicator: the result = half the amount of sulphite. Three hundred c.c. of saturated mercuric chloride are now added, also a little sodium chloride, and the liquid titrated with N 15-sodium hydroxide until again neutral; the result = total sulphur dioxide. After making allowance for the normal sulphite, the acid sulphite is obtained.

If *thiosulphate* is also present, the sulphite is first titrated with N 5-hydrochloric acid, with methyl-orange as indicator. After adding phenolphthalein, the solution is titrated with N 5-sodium

hydroxide until neutral; the result is total sulphur dioxide, and the acid sulphite is then found by difference. To another 50 c.c. of the solution is now added an excess of mercuric chloride, also 1 gram of sodium chloride, and the hydrogen chloride liberated is titrated, after adding 30 c.c. of 4*N*-ammonium chloride, with  $N/5$ -sodium hydroxide, with methyl-orange as indicator. After deducting the alkali necessary for the neutralisation of the acid sulphite, the result = thiosulphuric acid. L. DE K.

**Iodometric Estimation of Persulphuric Acid.** ERICH MÜLLER (*Zeitsch. anal. Chem.*, 1913, 58, 299—303).—The following process is recommended in the absence of hydrogen peroxide. Twenty c.c. of persulphate solution (about 0.36 gram of solid salt) are added to 25 c.c. of *N*-sodium hydroxide containing 1 gram of potassium iodide, and after waiting for at least five hours the liquid is acidified with 2*N*-sulphuric acid; the iodine liberated, which represents the available oxygen, is then titrated with thiosulphate as usual.

The reaction may be accelerated by heating the alkaline mixture for ten to twenty minutes on the water-bath. L. DE K.

**Colour Reaction for the Detection of Thiosulphates.** M. EMMANUEL POZZI-ESCOFF (Bull. Soc. chim., 1913, [iv], 13, 401—402).—To 1 or 2 c.c. of the solution to be tested, an equal amount of a 10% solution of ammonium molybdate is added, and 5 c.c. of sulphuric acid are poured carefully down the side of the tube to form a separate layer, when, if a thiosulphate is present, a bluish-coloured zone forms between the two liquids. The test will detect 0.0005 gram of sodium thiosulphate. T. A. H.

**Occurrence of Selenium in the Mother Liquors from the Preparation of Sulphite Cellulose.** PETER KLASON and HJALMAR MELLQVIST (*Arkiv. Kem. Min. Geol.*, 1913, 4, No. 34, 1—10).—The qualitative detection and quantitative estimation of selenium in the mother liquors from the preparation of sulphite cellulose is made difficult by the colour of these liquors, due to the organic substances present, and by the quantity of calcium salts present. After numerous experiments the authors recommend the following method. Three to five litres of the liquor, in portions of one litre at a time, are evaporated in an air-bath until the free sulphur dioxide is expelled. As soon as calcium sulphite begins to separate, sufficient hydrochloric acid is added to dissolve the crystals. This process is repeated from time to time until the volume of liquid is 200—300 c.c., when it is transferred to a smaller vessel of appropriate size, taking care to transfer any selenium which may have precipitated out. The solution is then strongly acidified and boiled to remove the last traces of sulphur dioxide, after which stannous chloride is added, and the solution again boiled for a few minutes. After keeping in the warm for one to two days, the selenium has settled to the bottom of the containing vessel, and can be filtered off and estimated according to the method previously described (A., 1912, ii, 201, 990). The presence of selenium is indicated by

the fact that it forms a red deposit on the sides of the combustion tube whilst the organic matter is being burned off.

Experiments made by the authors show that no matter how carefully the gases from the pyrites burners are washed and cooled, the selenium oxide contained in them cannot be completely removed.

T. S. P.

**Direct Estimation of Gaseous Nitrogen by means of Calcium Carbide.** R. NATTS (*Zeitsch. anal. Chem.*, 1913, 52, 265—292).—A special apparatus is described, in which a gaseous mixture containing nitrogen is passed over a red-hot mixture of 10 parts of calcium carbide and 1 part of fused calcium chloride. The operation is carried out in an atmosphere of hydrogen, using a porcelain boat.

The mass, which absorbs practically all the nitrogen if precautions have been taken to ensure absence of moisture, readily yields it as ammonia on treatment with sulphuric acid and a drop of mercury (Wilforth's modified Kjeldahl process).

The calcium carbide should be purified by heating in a current of hydrogen. As it generally contains some nitrogen, this should be estimated and allowed for.

L. DE K.

**Estimation of Ammonia by Titration.** LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1913, 26, 231—232).—Instead of absorbing the ammonia in excess of sulphuric or hydrochloric acid and titrating back the excess, the author recommends that a solution of boric acid be used. The ammonia can then be titrated directly with standard hydrochloric acid, using methyl-orange or Congo-red, preferably the latter, as indicator, the colour change being quite sharp.

In an ordinary Kjeldahl nitrogen estimation about 5 grams of boric acid in 100 c.c. of water should be used to collect the ammonia; no condenser is necessary. For very accurate work it is advisable to take a saturated solution of boric acid, add one drop of ammonium hydroxide solution, then sufficient indicator to give a colour, and finally run in 0.1N-hydrochloric acid until the colour change occurs; this solution is then used to absorb the ammonia.

T. S. P.

**Apparatus for the Distillation of Ammonia in the Kjeldahl Process.** G. DELATTRE (*J. Pharm. Chim.*, 1913, [vii], 7, 395—397).—A "baffle," consisting of a loose siphon tube of special form, is inserted in the leading tube from the distilling flask. This serves to break any bubbles which form in the tube, so that the distillation can be conducted more rapidly than in the forms of leading tube in general use. The apparatus is figured in the original. T. A. H.

**Detection and Estimation of Ammonia in Cerebro-spinal Fluid.** PIERRE THOMAS (*Bull. Soc. chim.*, 1913, [iv], 13, 338—400).—It is shown that the colour reaction already described (A., 1912, ii, 991) is suitable for the detection of ammonia in cerebro-spinal

fluid, since it is not affected by the presence of proteins or sugars. The amount of ammonia present may be estimated colorimetrically.  
T. A. H.

**Detection of Nitrous Acid in the Presence of Ferric Salts [in Waters].** PAUL ARTMANN (*Chem. Zeit.*, 1913, 37, 501). To 100 c.c. of the sample are added 8 grams of crystallised disodium hydrogen phosphate, and 0.2 gram of potassium iodide is then added. Five c.c. of 4N-sulphuric acid are added, and 2 c.c. of starch solution.

If nitrites are present, even in minute quantities, a blue coloration is noticed.  
L. DE K.

**Influence of Chlorine on the Determination of Nitrates by the Phenoldisulphonic Acid Method.** ROBERT STEWART and JOSEPH E. GREAVES (*J. Amer. Chem. Soc.*, 1913, 35, 579-582). In an earlier paper (A., 1910, ii, 652) it has been shown that the estimation of nitrates in soil extracts by the phenoldisulphonic acid method is affected by the presence of chlorides. It has now been found that accurate results can be obtained in such cases by means of the lime method proposed by Lipman and Sharp (*Univ. Calif. Publ. in Agric. Sci.*, 1912, 1, 12). Chloroform is sometimes added to the soil extract to inhibit the action of bacteria. In the case of extracts prepared by the lime method, however, reaction takes place between the calcium hydroxide and the chloroform with formation of calcium chloride, and the use of chloroform is therefore excluded.  
E. G.

**The Quantity of Nitric Acid Present in Fruit Juices, and Fruit Juice Statistics for 1911 and 1912.** JOSEF TILLMANS and ARTHUR SPLEITGERDER (*Zeitsch. Nahr. Genussm.*, 1913, 25, 417-422). -Fruit juices contain small quantities of nitric acid, the quantity being usually less than 1 mg. (N<sub>2</sub>O<sub>5</sub>) per litre. Two samples examined, one a raspberry juice and the other a strawberry juice, contained 5 mg. per litre, but this may have been due to the berries having been washed with water containing a large quantity of nitrate. Apart from this source of contamination, the presence of considerable quantities of nitric acid in fruit juices affords no indication or suspicion that water containing nitrates has been added to the juice. The diphenylamine sulphuric acid method was employed for estimating the nitric acid, and the process employed, preferably, after the juice had been treated with activated charcoal to remove interfering substances (compare A., 1913, 236), and then cooled by means of a freezing mixture. It is not advisable to cool the reagent before adding it to the liquid, as in certain cases the treatment with animal charcoal may be sufficient to provide both the reagent and juice are strongly cooled.  
Tables are given showing the chemical composition of the fruit juices examined during the years 1911 and 1912.  
W. B. S.

**Estimation of Phosphorus in Ferro-tungsten, Metallic Tungsten Powder, Tungsten Oxide, and Tungstic Acid by Direct Solution.** CHARLES M. JOHNSON (*J. Ind. Eng. Chem.*, 1913, 5, 297--298).—Ferro-tungsten is heated with concentrated nitric acid and hydrofluoric acid, then evaporated, dissolved in hydrochloric acid, again evaporated, and the greater part of the tungsten separated by filtration. The filtrate is then evaporated with nitric acid, and the residue repeatedly treated with nitric acid and evaporated, insoluble substances being separated by filtration. The phosphorus is, finally, obtained in nitric acid solution, and is precipitated by the addition of molybdate solution after the solution has been treated with potassium permanganate and the manganese dioxide dissolved by the addition of ferrous sulphate. Tungsten ores are first treated with hydrochloric acid and potassium chloride, and the phosphorus subsequently obtained in nitric acid solution. Metallic tungsten powder must be converted into oxide by roasting before the phosphorus is estimated, as in the case of ores, whilst tungstic oxide and tungstic acid are treated directly with hydrochloric acid and potassium chloride and afterwards with nitric acid.

W. P. S.

**Removal of Phosphoric Acid by means of Metastannic Acid in Qualitative Analysis.** WERNER MICKLEBURG (*Zeitsch. anal. Chem.*, 1913, 58, 293--298).—To the solution, which should be practically free from chlorine but contain 15 vol. % of nitric acid, is added a sufficiency of metastannic acid, and the whole is boiled for fifteen minutes. In this way the phosphoric acid is completely removed, and the filtrate is then analysed as usual.

The metastannic acid is prepared in the form of paste as follows: 150 grams of granulated tin are introduced into a cooled (0°) mixture of 750 c.c. of nitric acid (1.13) and 750 c.c. of water, and when all is dissolved, the liquid is poured into 10 litres of water. The deposit is washed, first by decantation and then on a filter, and bottled moist.

Besides phosphoric acid, the deposit may also retain iron and titanium; the first is tested for with ferricyanide, the latter with hydrogen peroxide. Surely any tin passes into solution.

L. DE K.

**Detection and Estimation of Arsenic by the Marsh Apparatus.** GEDRON MEILLERE (*J. Pharm. Chim.*, 1913, [vi], 7, 425--431).—The author describes the manner in which he carries out this process. He employs zinc, which has been treated with platinum chloride or copper sulphate, for evolving the hydrogen; on leaving the evolution flask, the gases are passed through a tube containing zinc, and then through a tube containing anhydrous sodium sulphate or sodium phosphate; the end of the capillary in which the arsenic mirror is collected is bent downwards and immersed in silver nitrate solution in order to ascertain whether any of the arsenic has escaped being deposited in the capillary. In the case of comparatively large quantities of arsenic, the capillary



may be replaced by a weighed tube containing copper foil on which the arsenic is collected and weighed, or the gases may be passed into silver nitrate solution and the quantity of arsenic estimated gravimetrically.

W. P. S.

**Modification of the Liebig Combustion Furnace.** HUGO BRACH and EMIL LENK (*Zeitsch. angew. Chem.*, 1913, 26, 230—231).—An ordinary Liebig combustion tube is surrounded by a wider tube, which is also packed with copper oxide over a length corresponding with that taken up in the inner tube. The inner tube is connected in the usual way with a sulphuric acid tube and a soda-lime tube, and leading from the latter is a length of tubing opening into the outer concentric tube at the end nearest the oxygen gas-holder. At the other end of this outer tube are fitted a soda-lime tube, a calcium chloride guard-tube, and a sulphuric acid bubbler.

A combustion can be completed in about half an hour, any carbon monoxide escaping from the inner tube being completely oxidised to carbon dioxide in the outer tube.

T. S. P.

**Estimation of Zinc in Ores.** D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1913, 5, 302—304).—The method proposed depends on the fact that ammonium carbonate separates zinc (and copper) from iron, aluminium, manganese, lead, and cadmium; the zinc and copper remain in solution, and the former is titrated with ferrocyanide after the copper has been precipitated as sulphide. One gram of the ore is heated with 5 c.c. of hydrochloric acid, D 1.12, 20 c.c. of concentrated nitric acid are then added, and the heating is continued until all brown fumes are expelled. After the addition of 1 gram of potassium chlorate, the mixture is evaporated to dryness, and the residue is treated with 50 c.c. of hot water and 0.5 gram of potassium hydroxide; 6 grams of ammonium carbonate are now added, the mixture is boiled for a few minutes, and the solution filtered, the insoluble portion being washed with hot 5% ammonium carbonate solution. The insoluble portion is then dissolved in hydrochloric acid, potassium nitrite added to reduce manganese dioxide which may be present, the solution neutralised with potassium hydroxide, and again treated with ammonium carbonate. The united filtrates and washings are acidified with hydrochloric acid, 20 c.c. of concentrated hydrochloric acid are added, the solution is heated to 70°, and the copper precipitated as sulphide. When the copper is practically all precipitated, 20 c.c. of ammonia (1:1) are added, and hydrogen sulphide is passed through the solution for a further short period. The zinc is then titrated at 70° with standardised potassium ferrocyanide solution, without previous removal of the copper sulphide.

W. P. S.

**Method for the Qualitative Analysis of the Zinc Group** RICHARD EDWIN LEE, ROY H. FRUINGER, and FRANK O. AMOS (*Am. Chem. Soc.*, 1913, 35, 566—579).—The methods usually employed for the qualitative analysis of the zinc group are discussed.

and various inaccuracies are pointed out. The complete precipitation of zinc, manganese, nickel, and cobalt can be effected by passing hydrogen sulphide into a weak, ammoniacal solution. By this means, the dissolving of the nickel sulphide is prevented, and the nickel is but rarely precipitated in the colloidal condition. The method renders it possible to precipitate and detect 0.0005 gram of any metal of the group in presence of large quantities of any or all of the other metals. Methods are also proposed for the subsequent analysis of the group precipitates, which are capable of confirming the presence of any of the metals even in quantities of 0.0005 gram.

E. G.

**Some Quantitative Separations of Neodymium.** TODD O. SMITH and CHARLES JAMES (*Chem. News*, 1913, 107, 205—206; *J. Amer. Chem. Soc.*, 1913, 35, 563—566).—Quantitative separations of neodymium from titanium, glucinum, uranium, and barium may be made by precipitating the neodymium as oxalate from boiling solutions. Oxalic acid is used as the precipitant, and after precipitation the solution is digested until the precipitate becomes granular.

In the separation of neodymium from zirconium according to the above method, the results are slightly high, some of the zirconium probably being carried down with the neodymium, zirconium oxalate being insoluble in water, but soluble in an excess of oxalic acid.

T. S. P.

**Detection of Mercury in "Kyanised Wood."** CHARLES GROFFIER (*Bull. Soc. chim. Belg.*, 1913, 27, 137—138).—The mercury sulphide obtained in due course after submitting the wood to the well-known destruction process of Fresenius and Ballo still contains organic matters which render the further identification of the mercury a matter of great uncertainty.

The author overcomes this difficulty by boiling the well-washed precipitate with dilute nitric acid (2:1). This removes the foreign matters. The residue is dissolved in aqua regia, and the usual reactions will then be obtained readily.

• L. DE K.

**Precipitation of Aluminium Hydroxide and its Separation from Chromium.** W. JAKÓB (*Bull. Acad. Sci. Cracow*, 1913, 1, 56—62).—Alumina may be obtained as a dense precipitate, readily washed, by adding to the aluminium salt solution (about 0.2 gram of the oxide in 100 c.c.) sufficient aqueous sodium hydroxide to redissolve the precipitate and then boiling with addition of excess of bromine water. Attention is called to the hygroscopic nature of the ignited precipitate.

Chromium, if present, is oxidised to chromate. The precipitated alumina must, however, be freed from adhering chromate by decanting the liquid and boiling the deposit with a solution of ammonium nitrate containing ammonia.

Traces of iron or magnesium do not interfere, but in the presence of sulphates or borates the method is less suitable.

• F. DE K.

**Estimation of Manganese in Irons and Steels by von Knorre's Process.** MAURICE HUYBRECHTS and N. JOASSART (*Bull. Soc. chim. Belg.*, 1913, **27**, 130—137).—A modification of von Knorre's process, ensuring a more complete precipitation of small quantities of manganese. Four grams (or less) of the sample are treated with about 50 c.c. of cold water, 7*N*-nitric acid (11 c.c. for each gram) is added, and the whole is heated for twenty to thirty minutes on the water-bath, when the last particles are dissolved by boiling for a minute. To the solution are now added 250 c.c. of water, 8 grams of ammonium persulphate, and 4 grams of sodium carbonate; after boiling for twenty minutes the manganese will be completely precipitated.

The precipitate is collected and drained (not washed). It is then dissolved in just a sufficiency of hydrochloric acid, boiled, and diluted. The iron is now precipitated by cautiously adding zinc oxide, the liquid is heated to nearly 100°, and then titrated as usual for manganese with standard permanganate. L. DE K.

**Colorimetric Method for the Estimation of Chromium in Steel.** FRANK GARRATT (*J. Ind. Eng. Chem.*, 1913, **5**, 298—300).—The process described by Koenig (A., 1911, ii, 337), which depends on the coloration which is produced when chromic salts are treated with sodium 1:8-dihydroxynaphthalene-3:6-disulphonate, is recommended as being trustworthy. Tungsten and molybdenum do not interfere with the process, but vanadium imparts a brown tinge to the pink chromic coloration. The red coloration given by titanium is destroyed on the addition of hydrofluoric acid or by strongly acidifying the solution with mineral acids. Concentrated sulphuric acid solutions of titanium, however, yield pink colorations with the reagent. W. P. S.

**Potassium Iodide and Mercurous Nitrate as a Delicate Reagent for Tungsten and Molybdenum.** M. EMMANUEL BOUÉ (*Revue. Bull. Soc. chim.*, 1913, [iv], **13**, 402—403).—The explanation of this reaction, described by Kofka (A., 1912, ii, 693), is that mercurous iodide is first formed, which is reduced to mercury by the excess of potassium iodide. The mercury then reduces the tungstate, producing the blue coloration. The reaction is given by sodium tungstate in presence of mercury and hydrochloric acid. In the case of molybdates the reaction is of very little value. If much molybdate is present, the mercury is oxidised by it, and a yellow precipitate of mercurous molybdate is formed. With dilute solutions, a pale blue, fugacious coloration is produced. T. A. H.

**Study of Certain Confirmatory Tests for Tin.** LEON J. CORMAN and MAX MOSHER (*J. Amer. Chem. Soc.*, 1913, **35**, 357—365).—The test for tin, which consists in reducing an acid solution of stannic chloride with an iron nail, and subsequently treating the stannous chloride with mercuric chloride, is not altogether trustworthy as usually carried out. It has been found that certain nails are not suitable because of the irregularity of their action.

The best procedure is to add one  $\frac{1}{2}$  inch cut nail to a total volume of 5 c.c. with an acidity equivalent to 2.5 c.c. of concentrated hydrochloric acid, and to heat for three minutes in a boiling water-bath. Under these conditions, 0.2 mg. of tin can be detected either alone or in presence of 250 mg. of antimony. When the amount of tin is small, a blank experiment must be made.

The ammonium molybdate test for stannous salts can be applied to stannic salt solutions after reduction with zinc. With a total acidity of 2.5 c.c. of concentrated hydrochloric acid in a volume of 10 c.c. the test is capable of detecting 0.01 mg. of tin in the absence of antimony, or 0.05 mg. in presence of 250 mg. of antimony. The presence of 5 mg. of antimony does not affect the sensitivity of the test.

E. G.

**The Electrolytic Separation of Tin and Tungsten.** W. D. THREAWELL (*Zeitsch. Elektrochem.*, 1913, 19, 381-384). The author gives a critical résumé of the processes of separation of tin and tungsten which are in use for quantitative purposes, including those of Donath and Müller (A., 1888, 531), Talbot (*Zeit. für Analyt. Chem.*, 1871, 10, 313), Rose, and Angenot (A., 1906, ii, 395). The two electrolytic methods of precipitating tin from ammonium sulphide and sodium sulphide solutions respectively are investigated by the author; he shows that with ammonium sulphide solution the deposited tin is generally contaminated with sulphur, and at times contains as much as 2 mg. of platinum. The deposit obtained from sodium sulphide solutions which contain a little free alkali are not so contaminated, particularly if the current is only allowed to pass for a very short time after all the tin has been deposited. From these experiments he has devised the following method for quantitatively separating tin and tungsten. The anode consists of a cylinder of platinum gauze, 35 mm. diameter and 140 mm. high. The anode is a cylinder of platinum foil, 41 mm. diameter and of the same height as the cathode; this is perforated by a number of holes to avoid the presence of a dead space at the back of the anode. The cathode is generally arranged so that it can be rotated, but stationary cathodes may be employed. The solution, which contains 100 mg. of tin and 1 gram of tungsten, is made up with 5 grams of pure sodium sulphide and 10 c.c. of commercial sodium hydroxide solution, which has been made alkaline with sodium hydroxide. The electrolysis is then carried out with a current strength of up to 1.7 amperes and a potential P.D. of 2.7 volts, the temperature being preferably between 50° and 60°. The current may be allowed to pass for 15 minutes after the deposition of tin is required for the separation of all the tin has passed through. If molybdenum is present, the results are not likely to be affected, since it does not deposit. Attempts were made to effect the separation from oxalic acid solution, but there was found to be a solubility of the tungsten deposit with the tin.

J. F. S.

**Rapid Methods for the Estimation of Antimony.** H. MEISSNER (*Zeitsch. analyt. Chem.*, 1913, 81, 16-18). The method

of antimony by potassium bromate and indigotin (A., 1903, ii, 697; 1904, ii, 292) may be employed as a rapid method, and in the separation of arsenic and antimony. Other known methods are described.  
C. H. D.

**The Direct Estimation of Caoutchouc as Tetrabromide.** F. WILLY HIRICHSEN and ERICH KINDSCHER (*Zeitsch. anorg. Chem.*, 1913, 81, 70-82).—The direct estimation of caoutchouc by means of bromine is liable to a number of errors, and experiments have now been carried out to determine the sources of error. The proportion of bromine in the product increases with the time of reaction at the ordinary temperature, but is almost constant when the reaction is carried out in chloroform solution cooled by ice. This method is also applicable to vulcanised rubber, which is readily dissolved by a solution of bromine in chloroform, even in presence of large quantities of inorganic matter.

In the analysis of the bromides obtained in these experiments, the solution in chloroform is precipitated by means of light petroleum, and the precipitated bromide is washed, first with alcohol and then with hot water and dried, and then fused with a mixture of sodium and potassium carbonates below a red heat.  
C. H. D.

**Estimation of Phenols in "Creolines."** ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1913, 27a, 128-129).—Two hundred and fifty c.c. of the sample of creoline ("soluble cresote") are treated in a separating funnel with 500 c.c. of water, acidified with sulphuric acid, and 100 c.c. of benzene added. After twenty-four hours, the supernatant liquid is submitted to distillation until the temperature rises above 240°. The distillate, which contains, beside the benzene added, the phenols and part of the hydrocarbons, is then shaken three times in succession with 50 c.c. of 10% sodium hydroxide. The united liquids are acidified with dilute sulphuric acid, and the phenolic layer is measured in a graduated tube; 1 c.c. may be taken to represent 1.055 gram.  
L. DE K.

**The Heat Test.** ALFRED C. EGERTON (*J. Soc. Chem. Ind.*, 1913, 32, 331-341).—The author has submitted the heat test to an exhaustive examination in the case of gun-cotton, nitroglycerin, and cordite. The theory of the connexion between the time of colouring of the indicator and the concentration of nitrogen peroxide in the heat test-tube is also discussed (compare Robertson and Smart, *Ibid.*, 1910, 29, 130).

The details and results of the many experiments carried out do not admit of a short summary; the author, however, emphasises the following points: To obtain a trustworthy and satisfactory stability test by which the actual tendency of the explosive to decompose can be accurately measured, it is necessary to carry out a continuous test, the results of which should be plotted graphically. The paper indicator usually used is open to certain errors, to obviate

which the author has devised a drop test. A solution of a naphthylamine and sulphanilic acid in acetic acid is placed in a small cell supported at the top of the heat test-tube. The time necessary for this to colour to a standard tint, under the action of the nitrogen peroxide evolved from the explosive, forms the new drop test. It is said to be simpler than the ordinary heat test.

A single heat test is untrustworthy and therefore valueless, because of the nitric acid formed in the explosive during the test. The author is of the opinion that a state of equilibrium is attained during a continuous test, and hence the value of this test.

T. S. P.

**Improved Apparatus for the Estimation of Carboxyl Groups in Organic Acids.** WILLIAM H. HUXTER and J. D. EDWARDS (*J. Amer. Chem. Soc.*, 1913, **35**, 452—461).—Fuchs (A., 1889, 463) has described a method for estimating carboxyl groups, which depends on the fact that organic acids liberate hydrogen sulphide from solution of potassium hydrogen sulphide saturated with hydrogen sulphide. An account is now given of an improved form of apparatus for carrying out the estimation.

A wide-mouthed reaction vessel is fitted with a rubber stopper with three holes. In one hole is placed a sample holder of the type used in the Victor Meyer vapour density apparatus. Another hole carries a tube for the admission of hydrogen sulphide, and fitted with a glass stopcock. In the third hole is inserted a three-way tap, enabling the reaction vessel and the air-chamber stand above it to be put into communication with one another or either of them to be opened to the air. On the outlet from this tap to the air is a narrow rubber tube provided with a pinchcock. A loose plug of glass wool is placed half-way down the air-chamber, and in the upper end is fitted a rubber stopper with two holes, one with a glass stopcock opening to the air, and the other bearing a delivery tube, without a stopcock, which is connected to the gas-burette.

The solution of potassium hydrogen sulphide is placed in the reaction vessel, and hydrogen sulphide is passed in until it is completely saturated and all the air has been expelled from the vessel. After the apparatus is ready, connexion is made between the reaction vessel, air chamber, and burette. The level of the water in the burette is noted, and the weighed sample of the organic acid is dropped into the reaction vessel. As the hydrogen sulphide is evolved, the level in the gas-burette must be followed closely by the levelling bulb. When the evolution ceases, the reading is taken, the reaction vessel shaken vigorously for three minutes, and the final reading noted. The weight of carboxyl ( $W$ ) is found by the following equation:  $W = V(b - w)0.00002632 / (1 + 0.00367t)$ , where  $V$  is the volume of gas evolved,  $b$  the barometric pressure, and  $w$  the vapour pressure of water at  $t^\circ$ .

Experiments are recorded which show that by this method monobasic organic acids give results 2.5% below the calculated, whilst dibasic acids yield results about 7% too high. E. G.

**Estimation of Formic Acid in Urine.** HENRY D. DAKIN, N. W. JANNEY, and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1913, 14, 341—354).—See this vol., i, 679.

**Solubility of Certain Metallic Salts of Volatile Fatty Acids in Organic Solvents. Application to the Qualitative Estimation of these Acids.** HENRI AGULHON (*Bull. Soc. chim.*, 1913, [iv], 13, 404—406).—A scheme for the detection of propionic, butyric, valeric, and hexoic acids is described depending on the fact that the cupric and ferric salts of these acids show increasing solubility and a greater range of solubility in organic solvents as the molecular weight of the acid increases. The corresponding salts of formic and acetic acids are insoluble in the organic solvents used.  
T. A. H.

**Estimation of Solid Fatty Acids by Hehner and Mitchell's Method.** HERMANN SERGER (*Zeitsch. öffentl. Chem.*, 1913, 19, 131—132).—A special filter for use in this method (A., 1897, ii, 289) is described. A Gooch crucible containing asbestos is fitted by means of a rubber ring into the top of a funnel, and the crucible and funnel are surrounded by a vessel containing ice. A flat dish filled with ice forms a cover for the apparatus. After the Gooch crucible has been cooled for thirty minutes by means of the ice-jacket, the solution containing the stearic acid precipitate is passed through the filter, and, when the liquid has been removed as much as possible by a suction pump, the collected stearic acid is dissolved in 70% alcohol, the solution evaporated, and the residue weighed.  
W. P. S.

**The Estimation of Lactic Acid in Urine.** HIROMU ISHIHARA (*biochem. Zeitsch.*, 1913, 50, 468—482).—By means of Ryffel's process of distillation of urine with 50% sulphuric acid, and the titration of the aldehyde thus produced by Ripper's iodometric method, about four-fifths of the lactic acid present can be found. For urines containing sugar, the process is not applicable. To get accurate results, the acid must be extracted from the urine by ether. After precipitation of certain constituents of the former by phosphotungstic acid, the phosphotungstic acid is then precipitated by barium hydroxide, excess of the latter precipitated by carbon dioxide, and the urine then concentrated and extracted for twenty-four hours. The lactic acid thus extracted can be then estimated by a slight modification of the von Fürth and Charaxes method. Lactic acid is thus found to be a by no means negligible constituent of normal urine, which contains about 0.08 gram per litre.  
S. B. S.

**Estimation of Adrenaline**

H. ELLIOTT (*Proc. Physiol. Soc.*, 1913, xv—xvii; *J. Physiol.*, 1914, 35, 1—4).—See this vol., i, 674.











